TAMPEREEN TEKNILLINEN YLIOPISTO
TAMPERE UNIVERSITY OF TECHNOLOGY

JUHA-MATTI LEHTONEN

# OPIMIZATION OF THE FIRST COATING LAYER ON TOC-BASED COIL COATINGS

Master of Science thesis

Examiner: prof. Petri Vuoristo
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# ABSTRACT

**JUHA-MATTI LEHTONEN**: Optimization of the first coating layer on TOC-based coil coatings
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Traditional coil coated steel product consists of two layers of coating, which are applied on top of a pretreated hot-dip-galvanized steel coil. In other fields of industry the TOC coating method is quite widely used and it has attracted attentions also in the coil coating industry. The economically and environmentally sound alternative designed to replace the traditional pretreatment and the base coating layer has increased research and development of the TOC method.

Thin organic coatings in coil coating applications have been studied quite scarcely in SSAB. This thesis is a part of the HYBRIDS – Hybrid Materials program, which studies among other subjects the potential of the TOC-method. In this thesis the goal was to optimize a coating layer on top of two separate TOC-substrates. The objective of the thesis was to find the most suitable binder, film thickness and curing cycle combination for the first coating layer of the TOC based product. The chemistry of the studied binders was mainly based on polyester and PVdF chemistry. With isocyanate crosslinked binder system, a polyurethane-chemistry based binder was also introduced to the studies. With all of the previously mentioned binder systems, the film thicknesses and curing cycles were varied to test a wide variety of property combinations.

The optimization started with the results of the accelerated environment exposure testing, with which the first elimination of binders was based. The mechanical testing data was analyzed with statistical method ANOVA. With the statistical analyzing method the most potential binder, film thickness and curing cycle for each TOC was selected from both of the binder categories. The final products were compared to reference samples, which were treated with the same paint process. The samples used for the references were traditionally pretreated and untreated HDG-steels. The final conclusions on the optimized products were done based on accelerated environment exposure testing and mechanical testing.

With the optimization process a clear indication was observed, that the film thickness variations and binder selection affects the properties of the product significantly. The thickest dry films performed with best results. A significant difference was not observed with the curing cycles, but marginally better results were observed with double curing with the TOC 2 substrate. 70 % PVdF / 30 % PMMA ratio binders performed with best results with both of the TOC substrates. TOC 2 had significant difficulties with polyester-chemistry, which led to

a series of separate studies. Isocyanate (instead of melamine) crosslinked binder worked perfectly with the said substrate.

Accelerated humidity exposure testing results and mechanical resistance testing results reveal a significant importance of the pretreatment or TOC-layer. HDG steel with any sort of binder suffers a significant amount of damage and deterioration during exposure to humidity in elevated temperatures. Mechanical resistance results show a similar trend. The traditionally pretreated samples and TOC based samples, when compared against each other, showed notable but not significant differences on behalf of the TOC based samples. A conclusion from the testing in this thesis is that the TOC based product can perform at least as well as the traditionally pretreated product. Although the results are quite encouraging and positive for the TOC based products, the results are not unequivocal and can only be considered as a guideline towards future studies and research projects.

# TIIVISTELMÄ

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Perinteinen maalipinnoitettu teräsohutlevy koostuu kahdesta pinnoitekerroksesta, jotka maalataan esikäsitellyn kuumavalssatun teräksen päälle. Muilla metalliteollisuuden alueilla laajahkosti käytössä oleva TOC-pinnoitus on herättänyt kiinnostusta myös teräsohutlevyjen pinnoituksessa *coil coating* -menetelmällä. Uuden esikäsittelyn ja pohjamaalikerroksen korvaavan menetelmän taloudellisuus ja ympäristöystävällisyys on lisännyt tukimusta ja tuotekehitystä TOC-pinnoitteiden alalla.

TOC-pinnoitteita *coil coating* -sovelluksiin on tutkittu SSAB:lla verrattain vähän, joten HYBRIDS – Hybrid Materials projektin osana tämän työn tarkoituksena on optimoida kahden TOC-pinnoitteen päälle maalattavaa pinnoituskerrosta. Työn tavoitteena olikin löytää eri sideaineiden, kalvonpaksuuksien ja uunitussyklien joukosta kahdelle erilaiselle TOC-pinnoitteelle optimaalinen ensimmäinen pinnoitekerros. Testattavien sideaineiden kemia perustui pääasiassa polyesteri- ja PVdF-kemiaan. Joukossa oli myös isosyanaatilla silloitettu pinnoite, jolloin joukkoon saatiin mukaan polyuretaanikemiaan perustuva vaihtoehto. Jokaisen sideaineen kohdalla varioitiin kalvonpaksuuksia ja uunitussyklejä, jolloin saatiin tarkasteltua hyvin laajaa erilaisten ominaisuuksien kombinaatiota.

Ominaisuuskombinaation optimointi suoritettiin perustuen kiihdytettyjen olosuhdetestausten tulosten tulkinnalle, eliminoimalla joukosta selkeästi heikoimmat sideaineet. Mekaanisten testien tuloksia tulkittiin tilastollisen analyysin avulla. Tilastollisen analyysin avulla perusteltiin lopullisten sideaineiden ja kalvonpaksuuksien, sekä uunityssyklien valinta. Karsinnan jälkeen parhaita tuotteita verrattiin referenssinäytteisiin, joina toimivat perinteisen esikäsittelyn läpikäynyt sekä esikäsittelemätön teräsohutlevy. Referenssit maalattiin samoilla spesifikaatioilla kuin TOC-pinnoitetut näytteet. Lopullinen TOC-pinnoitteen suorituskyky pääteltiin kosteuskestävyyden ja mekaanisen kestävyyden perusteella.

Selkeitä ominaisuuksiin vaikuttavia tekijöitä löytyi niin sideaineen kuin kalvonpaksuuksien osalta. Paksuimmat kalvot toimivat työn testauksissa parhaiten. Uunitussykleillä ei havaittu selkeää merkitystä tuotteiden ominaisuuksiin. Sideaineiden osalta 70/30 suhteella tehty PVdF/PMMA-pinnoite sai parhaat tulokset molempien TOC-pinnoitteiden kanssa. Toisella TOC-pinnoitteella havaittiin selkeitä ongelmia polyesterikemian yhteensopivuuden kanssa, josta aloitettiin erillisiä tutkimusprojekteja. Isosyanaatilla silloitettu polyuretaanikemiaan pohjautuva sideaine toimi kuitenkin erinomaisesti kyseisellä TOC-pinnoitteella.

Kiihdytetyt olosuhde testaukset ja mekaaniset testaukset osoittivat selkeästi esikäsittely- tai TOC-kerroksen tärkeyden. Kuiva sinkki maalattuna millä tahansa sideaineella koki mittavat vahingot altistuessaan kosteudelle. Myös mekaaniset tulokset olivat selkeästi esikäsiteltyä ja TOC-pinnoitettua näytettä heikompia. Esikäsitellyn ja TOC-pinnoitetun näytteen välillä ei ollut yhtä selkeää eroa, mutta suuntaa-antava havainto paremmuudesta pystyttiin toteamaan. Johtopäätöksenä tuloksista voidaan todeta, että TOC-pinnoitettu näyte toimii vähintään yhtä hyvin, ellei jopa paremmin kuin esikäsitelty näyte. Tulokset ovat kuitenkin ainoastaan suuntaa-antavia ja tehty kohtuullisen pienellä otannalla, joten tämän työn perusteella ei voida yksiselitteisesti todeta TOC-pinnoitetun tuotteen paremmuutta perinteiseen esikäsiteltyyn tuotteeseen. Todetaan kuitenkin vielä, että tulokset näyttävät positiivisilta ja lisätutkimuksia aiheesta on syytä toteuttaa.

# PREFACE

This master´s thesis was completed at SSAB´s R&D in Hämeenlinna. I sincerely thank SSAB and my supervisor Product Development Manager Antti Markkula for giving me the opportunity to work with such an interesting subject and with such incredible people.

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Juha-Matti Lehtonen

# CONTENTS

# LIST OF SYMBOLS AND ABBREVIATIONS

| | |
|---|---|
| ALD | Atomic Layer Deposition |
| ANOVA | Analyze of Variance |
| BPA | Bisphenol A |
| BSS | Between-group sum of squares |
| C | Carbon |
| $CO_2$ | Carbon dioxide |
| CPVC | Critical Pigment Volume Concentration |
| DNNDSA | Dinonylnaphthalene disulfonic acid |
| DNNSA | Dinonylnaphthalene sulfonic acid |
| DP | Degree of Polymerization |
| ECH | Epichlorohydrin |
| EDS | Energy-dispersive X-ray spectroscopy |
| EN | EN-standard |
| EPMA | Electron probe microanalyzer |
| EU | European Union |
| F | Fluorine |
| F-ratio | F-distribution ratio (continuous probability distribution) |
| HDG | Hot-Dip-Galvanized |
| HDI | Hexamethylene diisocyanate |
| Hiarc | Registered brand name for high-end façade coating (Ruukki) |
| HMMM | Hexamethoxy methylmelamine |
| HYBRIDS | Research programme name for collaboration of Finnish industrial companies and research institutes |
| IPDI | Isophorone diisocyanate |
| MDI | Methylene diphenyl diisocyanate |
| MEK | Methyl Ethyl Ketone |
| NASDAQ OMX | American multinational financial service operating the stock market |
| NDT | Non-destructive testing |
| P | Phosphorus |
| PE | Polyester |
| pH | Measure of acidity or basicity |
| PIR | Polyisocyanurate |
| PMMA | Polymethyl methacrylate |
| PMT | Peak metal temperature |
| p-TSA | p-tolyene sulfonic acid |
| Pural | Registered brand name for high-end roofing coating (Ruukki) |
| Purex | Registered brand name for mid-end roofing coating (Ruukki) |
| p-value | Probability value |
| PVdF | Polyvinylidene fluoride |
| QCT | Accelerated humidity testing (Q-fogg condense tester) |
| RC-class | Corrosion resistance class |
| REACH | Registration, Evaluation, Authorization and Restriction of chemicals |
| RoHS | Restriction of Hazardous Substances |
| RSL | Restricted Substances List |
| RUV-class | UV radiation resistance class |
| RWS | Rainwater system |

| | |
|---|---|
| $ScCO_2$ | Supercritical carbon dioxide |
| SEM | Scanning Electron Microscope |
| Si | Silicon |
| SIMS | Secondary Ion Mass Spectrometry |
| $SiO_2$ | Silicon dioxide |
| SLIPS | Slippery Liquid-Infused Porous Surfaces |
| Sol-Gel | Method of producing solid coatings from small molecules |
| TDI | Toluene diisocyanate |
| Ti | Titanium |
| $TiO_2$ | Titanium dioxide |
| TOC | Thin Organic Coating |
| TP | Thermoplastic |
| TS | Thermosetting |
| TUT | Tampere University of Technology |
| UV-radiation | Ultraviolet-radiation |
| VAMS | Value added materials |
| VOC | Volatile Organic Compound |
| WSS | Within-group sum of squares |
| XRF | X-ray fluorescence |
| Zn | Zinc |

| | |
|---|---|
| $A$ | Area |
| $a$ | Thickness of the sample from the farthest crack |
| $b$ | Thickness of the sample (substrate, metal coating, organic coating) |
| $D$ | Shear rate |
| $F$ | Force |
| $l$ | Thickness of the film |
| $SFE$ | Surface Free Energy |
| $T$ | Surface tension |
| $t$ | Thickness of the sample without organic coating |
| $T_g$ | Glass transition temperature |
| $T_m$ | Melting temperature |
| $\eta$ | Viscosity |
| $\theta$ | Contact angle |
| $v$ | Velocity |
| $\tau$ | Shear stress |

# 1. INTRODUCTION

Continuous coating of metal coils is a fascinating and highly sophisticated method of giving new properties for metal substrates. With superior quality over post-finishing options, continuous coil coating is an ever-growing industry. Coil coating lines are easy to manage, environmentally sound, economical and versatile option in the field of coating metallic substrates with organic coatings. Coil coatings give great benefits to numerous of industrial applications including, but not limited to, roofing, indoor use and façades. Usually two different layers of organic coatings are used, a top coat and a primer coat. With additional pretreatment layer, proper adhesion and corrosion protection for the product is ensured.

In this thesis the focus is on the interface and adhesion of the pretreatment layer and the first layer of the coating system. As a part of the research program HYBRIDS, in this thesis a new product, that replaces the traditional pretreatment layer and the primer layer, is studied. Thin organic coating (TOC) is a potential new route in manufacturing multilayer coatings with a single run through the coil coating line. In coil coating products the new approach is still relatively unknown.

During the last few years, a laboratory scale research on different thin organic coatings has been done with a collaboration of SSAB, Top Analytica and the manufacturers of the thin organic coatings. Two of the most promising thin organic coatings were chosen to be a part of this thesis and further industrial research. The potential of the thin organic coatings as a replacement for traditional pretreatment layer and primer layer has been studied and promising results have been achieved. In the extensive experimental part of this thesis the most suitable and the most promising coating systems to be used with thin organic coatings are tested and studied. The emphasis is on the optimal first layer on top of the thin organic coating. A number of different combinations of film thicknesses, curing cycles and paints were used to determine the coating systems that show potential in future applications. Finally the most suited binders and other parameters were selected and a similar test cycle was administered for the final products, at this point also a reference of a traditional system was used.

This thesis is part of an ongoing five year project on the field of thin organic coatings and the reason for the study is to find potential binders and optimal parameters for the intermediate layer of the full coating system. Simultaneously a number of separate, but related, studies with thin organic coatings are underway. In this thesis also these separate studies are mentioned and discussed. In the theoretical part of this thesis the binders used in the experimental part are discussed, along with the theoretical background required to understand the interactions between the layers in the coil coated products.

# 2. COIL COATING IN SSAB

SSAB is a steel company that operates globally and is based in the Nordic countries and in the US. Through the share exchange in 2014 SSAB combined forces with Rautaruukki and started to operate under the name SSAB, thus becoming the leading steel company in the Nordic countries. The new SSAB has about 17 300 employees in over 50 countries. Annual production capacities are in the range of 8.8 million metric tons of steel. The new company is listed in NASDAQ OMX Stockholm and Helsinki. Net sales of the company were approximately 6.4 billion euros in 2013.[1], [2]

SSAB is divided into five divisions, which all specialize in different market segments. SSAB Special Steels is a global steel manufacturer and a service provider in value added Advanced High Strength Steels and Quenched & Tempered steels. SSAB Europe is a Nordic based steel producer of high quality strip, heavy plates and tubular products. SSAB Americas focuses on a steel production of high quality heavy plates and is based in North America. Tibnor is a full service distribution partner of SSAB´s steel products. Ruukki Construction is a provider of energy efficient building and construction solutions in Europe [1], [2]

This chapter gives the basic information about the coil coating process and a number of reasons for its use. The structure of the finished coil coated steel strip is discussed and a few examples of SSAB´s coatings are given.

## 2.1 Coil coating process

Color coated steels are a part of SSAB Europe´s product portfolio. Color coated steels are manufactured in Hämeenlinna, Kankaanpää, Borlänge and Finspång. Both cold rolled and hot dip galvanized steel strips are used in color coating lines. Approximately 98 % of the color coated products are hot dip galvanized steel strips due to the superior corrosion resistance compared to cold rolled strips. Basically cold rolled steel is coil coated only for indoor applications and some smaller more specific applications. Part of the color coating product family is laminated steel strips, which use prefabricated polymer films instead of paint. [3][4][5]

Coil coating is a way of continuously applying an organic coating with a roll-coater system on top of a cold rolled or metal coated steel strip. The process in general consists of cleaning, chemical pretreatment and the application of a single or multiple layers of liquid paint on either both sides or just one side of the strip. The final coating film is formed from the liquid paint via curing process in an oven. The coil coating line operat-

ing in Hämeenlinna is explained in more detail in the next subchapter 2.1.1 Coil coating line in Hämeenlinna. [4]

Prepainted steel is a viable and in numerous ways even superior option to post-finishing of the metal product. With highly automated and continuous coating process the quality of the paint finish far surpasses many other methods. The properties of the finished product are consistently high. The thickness and appearance of the paint films are uniform throughout the whole surface area of the coil. Tolerances of different properties are fairly narrow and the precise specifications result in good adhesion, durability, corrosion resistance and weathering resistance. [4]

The coil coating process has been optimized to be cost effective for both the coil coater and the end-user. Coil coating produces minimum material loss and uses energy efficient coating methods, also the pollution levels are far smaller than that of post finishing methods. New regulations through REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) enforced by EU (European Union) for different chemicals leads to more environmentally sound options in the coating process. The emissions, water and effluent treatment and disposal and VOC (Volatile Organic Compounds) use are well controlled. [4][6][7][8]

Pre-coated metals are used in a vast field of different applications. The most dominant field is construction sector with almost 75 % of the use of all color coated steel products. In this segment there are interior and exterior applications. Coil coated metal is mostly used in roofing, wall cladding, façades, doors, shutters, ceiling panels, RWS (rain water systems) and flooring. Applications in the field of transport takes about 6 % of the color coated products. Color coated metal sheets and panels are used in busses, tankers, trucks, various car parts, mobile homes, containers and railway vehicles. Domestic appliances and furniture together governs about 8 % of the use of pre-coated metal. Appliances such as refrigerators, freezers, washing machines, clothes driers, microwaves, dishwashers and cookers are made of coil coated steels. Heating and ventilation systems are often made of pre-coated steels, teletronics, non-stick bake ware, shelving, furniture and lockers among others are also prime applications for coil coated products. The rest of the coil coated products are used in smaller fields of application such as packaging, display boards and traffic signs. [3][4]

### 2.1.1 Coil coating line in Hämeenlinna

Hot dip galvanized and cold rolled steel coils are color coated in Hämeenlinna at the coil coating line. Color coated products are manufactured according to the requirements of EN 10169. The line can operate at the maximum line speed of 90 m/min with steel strips that are in the dimensions of roughly 450 to 1400 mm in width and 0.3 to 1.5 mm in thickness. Before the organic coating is applied on the steel surface a pretreatment

process is needed. Pretreatment process is illustrated in Figure 2.1, where the different parts of the process are marked as numbers 1 through 15. [3]

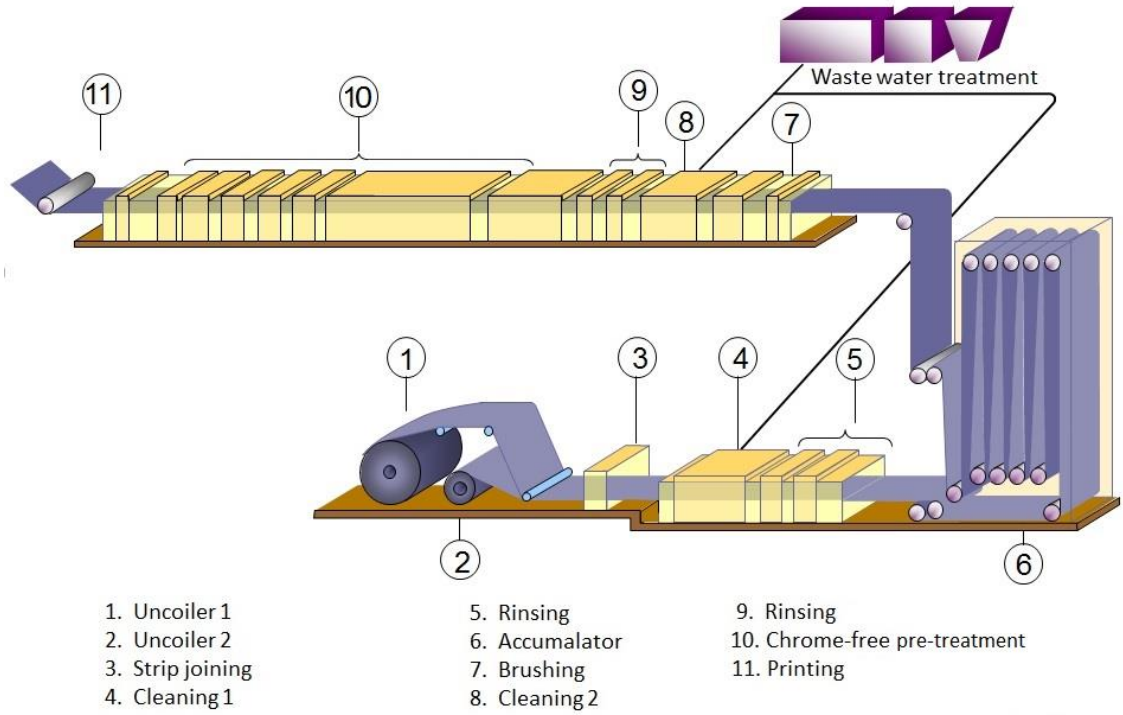


***Figure 2.1.*** *The pretreatment section of the coil coating line in Hämeenlinna (modified) [9]*

Pretreating the metal with two separate alkaline wash operations the excess aluminum oxides, oils, grease, metal particles and other impurities are effectively removed from the surface. Alkaline aqueous wash is done with heated (approximately 60 °C) sodium hydroxide in the pH range of 12-13. The reactions between the aqueous alkaline and the organic impurities cause the hydroxide ions to saponify the fats and oils and pickle the surface of the strip. The alkaline wash removes the aluminum oxides as well as frets the metallic zinc. After each wash cycles there is a hot water rinse in which the water-soluble reaction products are removed. Process water is used in the wash and rinse phases, except with the last rinse which is done with deionized water. [3][4]

Coil coating line in Hämeenlinna has moved to a completely chromate-free process due to the stringent environmental policy and the upcoming addition of chromate substances to the Restricted Substances List (RSL) governed by European Union. Instead of chromate passivation Hämeenlinna now uses titanium based pretreatment system. [6][7][10]

The native oxide layer of the substrate has effective anti-corrosive properties, but with the aim in high quality products it must be replaced by a similar layer, but with more controllable and desired properties. The chemically created protective layer is more uniform in thickness, has lower porosity, better transparency and higher electrical re-

sistance than the native layer, consequently leading to a higher degree of corrosion resistance. Adhesion promoters are also added to the layer to ensure adequate adhesion between the pretreatment layer and the paint layers. The titanium based pretreatment layer protects the substrate from mechanical and electrical corrosive media by acting as a barrier between the coating and the substrate. The final pretreatment layer is insoluble to water, chemically bonded to the substrate and has a gauge range of approximately 30-50 nm. [3][4]

With chrome-free systems there is no alkaline passivation. The barrier layer is done with a no-rinse process with aqueous titanium solution. The solution of hexafluorotitanic acid, fluorides, phosphoric acid and water soluble polymers is applied to the surface of the steel strip with a spray and squeeze (spray-squeegee) system illustrated in Figure 2.2. In the spray and squeeze system the pretreatment chemical is applied to the surface of the strip via series of nozzles. The excess chemical is removed with the squeegee roll and simultaneously the aqueous chemical is distributed evenly on the strip surface. Drying is done with approximately 50 °C hot air. The final chrome-free conversion coating consists of an oxide layer from the metals in the solution and the substrate with phosphorus in the oxide lattice and a surface film of the organic polymers. [4][11]

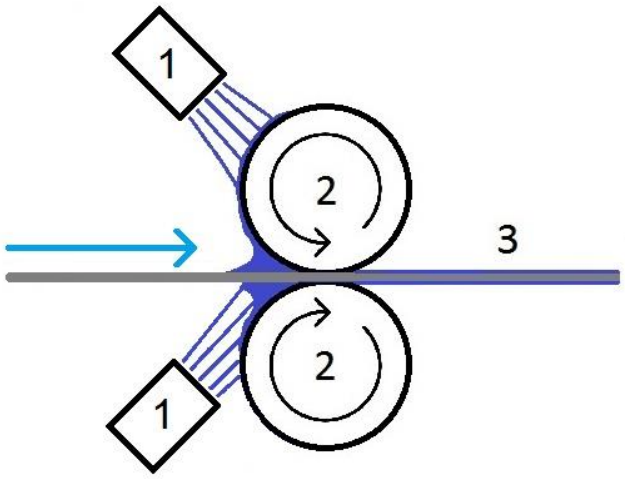


***Figure 2.2.*** *Spray and squeeze system*

The conversion coating is formed in two stages of chemical reactions. In the first stage the oxidization reactions governed by the pretreatment solution dissolve metallic ions from the surface of the substrate. In the second stage hydroxides and oxides are formed. The Ti- and Zn-oxides form a web-like structure on the surface of the substrate thus creating an impermeable barrier.[3][4]

The pretreatment process significantly increases the corrosion resistance of the final coating system; it also acts as an adhesion promoter for the following paint layers. After the pretreatment, the steel strip is painted using two separate coaters illustrated in the Figure 2.3. [4]

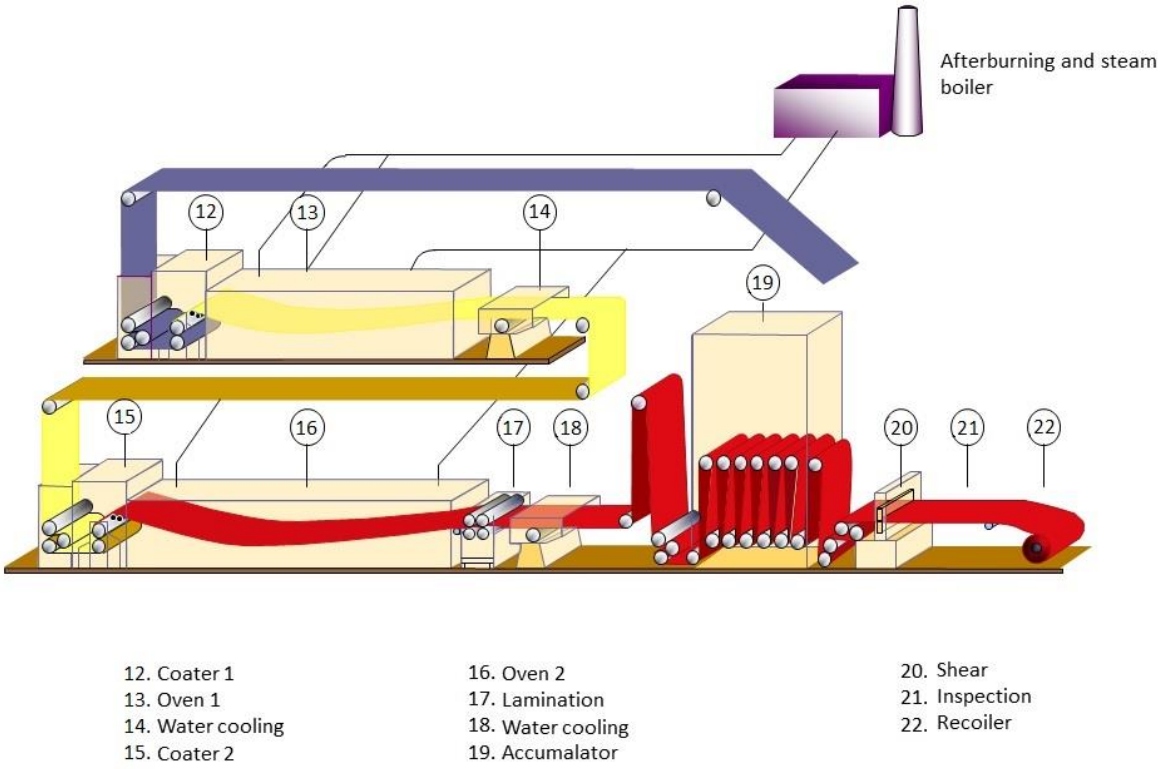


***Figure 2.3.*** *The second section of the coil coating line in Hämeenlinna (modified) [9]*

The first coater system in the coating line applies a primer on both sides of the steel strip. The primer is applied with a reverse roll coating method. The two-roll-coater uses a pick-up roll to wet the applicator roll with paint. The applicator roll rotates in the opposite direction of the steel strip thus coating the substrate with uniform layer of paint. The amounts of paint to be applied can be controlled with the roll speeds and the width of the gap between the rolls. Both sides of the substrate are coated with the above mentioned method. The curing of the primer is done in a 27 m long convection oven in which the solvents evaporate from the paint. The curing process has to be controlled closely to reach the desired quality for the coating. PMT-value (peak metal temperature), in which the curing process is optimal, is different for each coating and varies between 204-254 °C. [3][4][12]

After the curing of the first layer, the strip continues through water cooling, in which the temperature of the strip is lowered. After drying, the strip is coated with a second layer of paint called top coat. The second layer is applied with similar coater system as the primer, but a third roll is added to control the gauge of the top coat. The metering roll measures the right amount of paint on the applicator roll to control the thickness of the

paint film. The second coater also coats both sides of the steel strip; the bottom side is coated with a layer called the backing coat. The reverse roll coating method is illustrated in Figure 2.4. [3][4][9][12]

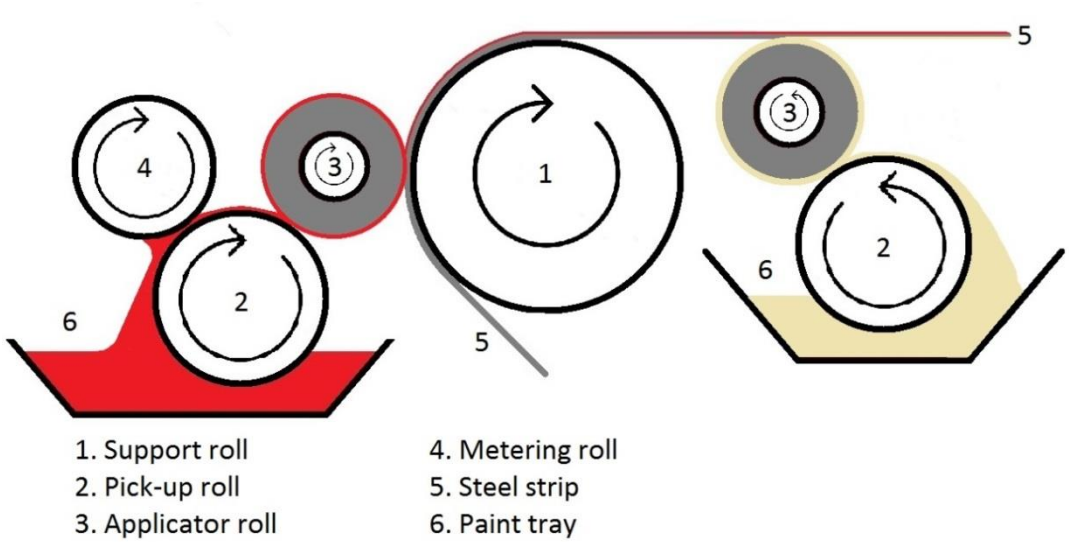


***Figure 2.4.*** *Reverse roll coater for top and backing coat*

The second curing process is done in a 37 m convection oven in which the solvents evaporate from the top coat and the backing coat. Cooling of the finished strip is done with a water cooling system similar to the one after the first curing process. After the cooling of the steel strip, the final product can be cut to desired lengths of coil. A protective film can be used on top of the finished coating to prevent mechanical damage to the coil in storage, during transport or further handling. Lamination process is also available in Hämeenlinna. In the lamination process adhesive glue is applied instead of the second paint layer. The adhesive glue activates in the convection oven and the laminate is applied to the surface with the use of additional roll system. [3][4]

## 2.2 Structure of the coating

Adequate protection for steel products, especially for exterior applications, cannot be obtained by a single layer of coating. Even though it is possible to build up very thick coatings (High Build Coatings), usually the final product has at least two layers of paint on both sides of the strip. The basic two layer coating structure consists of the steel substrate, zinc coating, pretreatment layer, primer and top/backing coat. The structure of finished product is illustrated in the Figure 2.5.

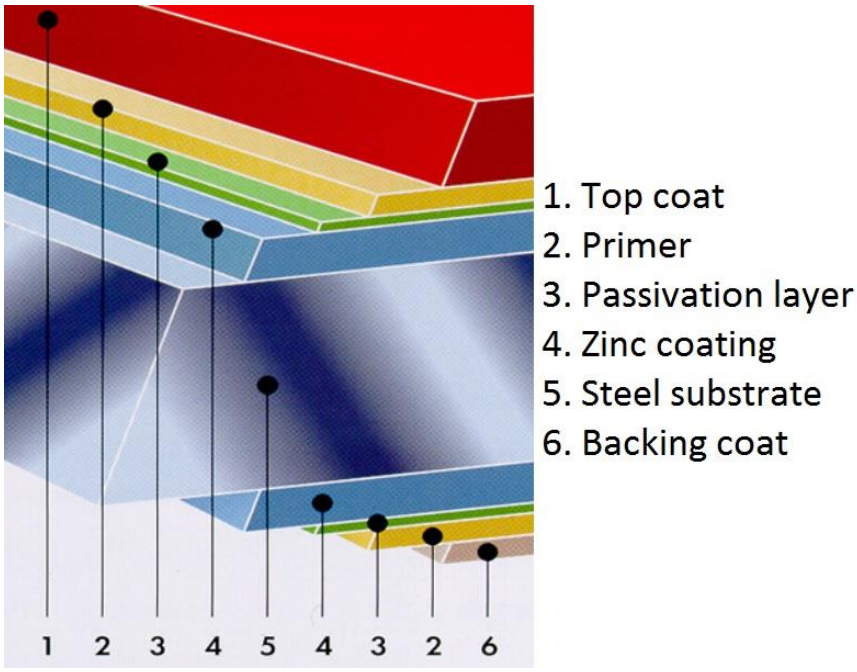


***Figure 2.5.*** *The structure of a two layer coil coating [9]*

The steel substrate is the base on which the coating is applied to protect the steel from corrosion. The steel strip substrate provides the basic mechanical properties and is the component that makes it possible to obtain and hold the wanted form of the product. The zinc coating in hot dip galvanized products is usually in the thickness range of 7-25 µm and it gives the steel a fair resistance to corrosion with cathodic protection. The pretreatment layer acts as a barrier for corrosive media and therefore gives additional protection against corrosion, as described in the previous subchapter 2.1.1 Coil coating line in Hämeenlinna. The pretreatment layer is less than 50 nm thick and it has good adhesion properties for the primer layer. The primer is approximately 5-20 µm thick and gives the coating system yet another addition to protection against corrosion and acts as a foundation for the top coat. The top coat gives the finished product its desired appearance and provides the whole system with the first line of defense against rain, snow, ice, sunlight and condensation. Top coat also provides the main abrasion resistance against mechanical stress such as scratches and dents. The reverse side of the finished product does not have to endure the same level of stress as the topside; therefore it does not have to possess as good properties as the top coat. In Hämeenlinna usually 7-10 µm thick epoxy based coatings are used as backing coats. The full coating system offers the steel substrate protection against environmental changes, additional properties and the desired appearance (color, gloss etc.). [3][13][14][15]

### 2.2.1 Coil coated product at SSAB

The new combined company of SSAB and Rautaruukki offers more solutions to the color coated steel market than either company did individually. Because the new and

improved product portfolio of color coated products has not yet been released, this thesis only presents the color coated products of the former Ruukki Metals Oy. Color coated product portfolio offers a wide variety of different color coatings for different environments and applications. The appropriate coating for specific application is chosen with a balancing act between the required quality and the costs of the coating. The continuous research and development has led to a comprehensive selection of coating options tailored for different purposes. Two different entireties have to be considered when choosing a coating for a specific application; the desired appearance and the desired performance. The following aspects govern the choice of the coating. Climatic conditions, indoor or outdoor location, mechanical, physical and chemical requirements, service life, appearance and price. [9][10][12]

The product portfolio consists of 24 different standard colors. All of the standard colors were carefully selected with the aid of architects to fit in with the Scandinavian building architecture. The whole product portfolio consists of about 200 different shades of color ready to be manufactured for customers. Customers can also order their unique color shade that will be developed to meet the requested standard. Different gloss properties can be obtained for the coating; available gloss options vary from high gloss to matt finishes. The structure of the coating surface affects both the appearance and the performance of the product. SSAB offers smooth, textured and structured finishes for the top coat as seen in Figure 2.6. [9][10][15]

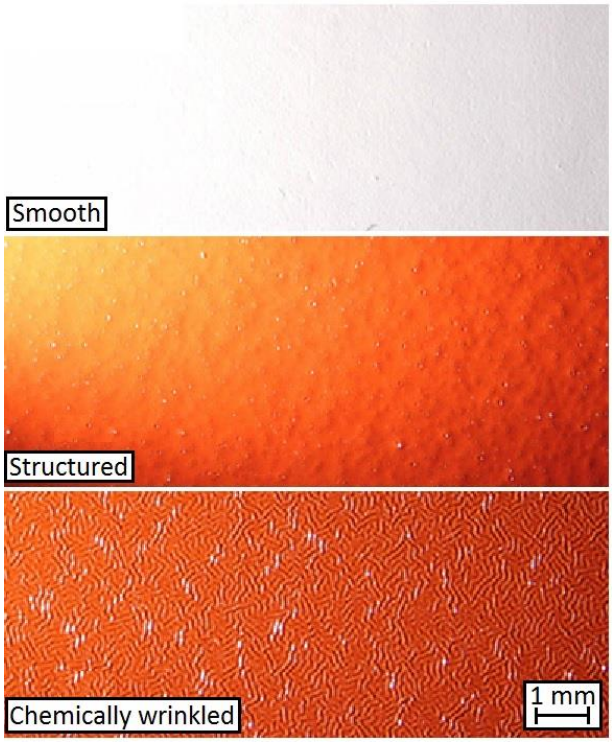


***Figure 2.6.*** *Surface patterns of coil coatings [15]*

The color coated products for outdoor applications are basically divided into two categories; roofing/RWS coatings and façade coatings. Roofing coatings include polyester, polyester matt, Purex, Pural and Pural matt. Coatings suitable for roofing must endure for example UV-radiation from the sun, corrosion media from water and impurities and different kinds of abrasion from ice and snow. For rain water systems the former Ruukki Metals tailored a special two sided Pural RWS. With its excellent formability and corrosion resistance Pural RWS is used in applications in which it has to endure significant forming and an aggressively corrosive environment. Coatings for façades include Hiarc, Hiarc matt, Hiarc max, Hiarc reflect and polyester. Façade coatings are tailored to have a high color durability, formability and corrosion resistance. Coatings that are applied to improve the appearance of buildings must be easy to clean and have a tidy and neat outlook. [9][10]

**Polyester** coatings are the most affordable and most widely used coating option, suitable for both roofing and façade applications. The properties of polyester coatings are naturally inferior to the more expensive coating options. Polyesters can be used in applications that are not subject to extreme conditions. Suitable uses for polyester coatings are warehouses, sandwich-panels, indoor applications and applications that are not designed to have a long service life. The properties of polyester coatings can be modified relatively effortlessly, but the modest UV radiation and corrosion resistance restrict its use to limited applications. [3][10][16]

**Purex** coatings were developed especially for roofing profiles and construction sheets to be used in fairly demanding conditions. Purex is the mid-quality solution in the coating hierarchy. Purex coatings outperform polyester coatings, but are surpassed in quality by Pural coatings. Purex is considered to be the coating solution that gives excellent properties with reasonable price. [10][17]

**Pural** is a polyurethane based coating solution that possesses excellent corrosion resistance properties. The good formability of Pural coatings makes it also a prime choice in rain water systems. Pural is used widely in roofing applications and due to its excellent performance in demanding conditions it is the high-end product in the coating hierarchy. [10][18][19]

PVdF based **Hiarc** coatings possess excellent UV radiation resistance properties; they are practically stable under UV radiation. Polyvinylidene fluoride based coatings are especially developed for façade applications because they uphold their appearance even under extreme conditions and are well resistant to corrosion. The low surface energy of the coating provides excellent dirt pick-up properties.

The basic properties of the above mentioned roofing and façade coatings are presented in Table 2.1. and Table 2.2.

***Table 2.1.*** *Properties of former Ruukki Metals´ different roofing coatings (modified) [20]*

| | | Coating | | | | |
|---|---|---|---|---|---|---|
| | | **Pural** | **Pural matt** | **Purex** | **PE** | **Pural RWS** |
| **Property** | Coating thickness (µm) | 50 | 50 | 26 | 25 | 40 |
| | Coating embossing | Structured | Structured | Structured | Smooth | Structured |
| | Gloss (Gardner 60 °) | 40 | 3-5 | 7 | 35 | 40 |
| | Minimum bending radius | 1t | 1t | 1t | 3t | 1t |
| | Lowest forming temperature ($^{o}$C) | -15 | -15 | -15 | 0 | -15 |
| | Max operating temperature ($^{o}$C) | 100 | 100 | 100 | 100 | 100 |
| | RUV-class * | RUV4 | RUV4 | RUV3 | RUV2 | RUV4 |
| | RC-class ** | RC5 | RC5 | RC4 | RC3 | RC4 |
| | Scratch resistance (g) | >4000 | >4000 | >2500 | >2000 | >3000 |
| | Dirt pick-up | Excellent | Excellent | Excellent | Good | Excellent |
| | Solvent resistance | Good | Good | Good | Good | Good |
| * UV radiation resistance class RUV4 being the best, RUV1 being the worst<br>** Corrosion resistance class RC5 being the best, RC1 being the worst | | | | | | |

***Table 2.2.*** *Properties of former Ruukki Metals´ different façade coatings (modified) [20]*

| | | Coating | | | | |
|---|---|---|---|---|---|---|
| | | **Hiarc max** | **Hiarc** | **Hiarc matt** | **Hiarc reflect** | **PE** |
| **Property** | Coating thickness (µm) | 40 | 27 | 27 | 27 | 25 |
| | Coating embossing | Smooth | Smooth | Structured | Structured | Smooth |
| | Gloss (Gardner 60 °) | 35 | 35 | 3-5 | 40 | 10-90 |
| | Minimum bending radius | 1t | 1t | 1t | 2t | 3t |
| | Lowest forming temperature ($^{o}$C) | -10 | -10 | -10 | -10 | 0 |
| | Max operating temperature ($^{o}$C) | 110 | 110 | 110 | 110 | 100 |
| | RUV-class * | RUV4 | RUV4 | RUV4 | RUV4 | RUV2 |
| | RC-class ** | *** | RC4 | RC4 | RC4 | RC3 |
| | Scratch resistance (g) | > 3500 | > 3000 | > 3000 | > 2500 | > 2000 |
| | Dirt pick-up | Excellent | Excellent | Excellent | Excellent | Good |
| | Solvent resistance | Good | Good | Good | Good | Good |
| * UV radiation resistance class RUV4 being the best, RUV1 being the worst<br>** Corrosion resistance class RC4 being the best, RC1 being the worst<br>*** Extremely demanding conditions (marine locations) | | | | | | |

There are numerous of other coatings and laminates that are manufactured by SSAB, but the above mentioned are the most commonly used and represent the low-, mid- and high-end quality in the coating hierarchy. This thesis studies the first layer of the coating system where the currently used pretreatment layer is replaced with a thin organic coating (TOC) and the paints selected for the study are polyester, polyurethane and polyvinylidene fluoride based.

# 3. HYBRIDS – HYBRID MATERIALS PROGRAM

This thesis is part of an ongoing research program called HYBRIDS. The HYBRIDS programme is a collaboration of Finnish industrial companies and research institutes and it is funded by the Finnish Funding Agency for Technology and Innovation (TEKES). The aim of the program is to create a unique multidisciplinary competence and technology platform to boost the competitiveness of Finnish companies. HYBRIDS program focuses on knowledge-intensive high technology products e.g. value added materials (VAMs). The aim of the projects linked to HYBRIDS is to use co-operation of academia and industry to combine scientific knowledge with critical future needs of the industry. Eventually the goal is to create a new type of research and business ecosystem, which will be beneficial to Finnish companies. [21]

The priorities and goals of the above mentioned programme are to combine and use common engineering materials in an innovative way. To improve the properties and reduce the time to market and life cycle costs of the new hybrid materials. Use and stretch the application limits of commercially cheaper basic materials in a more demanding applications. Extend and improve the available engineering material section and product design processes. Finally there is a goal to generate applicable design relevant material property data for hybrid materials, composites and coatings. [21]

HYBRIDS program is divided into five industry focused projects. All projects have an emphasis on engineering hybrid material solutions with more than a single functionality. The projects are listed as follows, P1. Multifunctional thin coatings, P2. Multifunctional thick coatings and composites, P3. Light multifunctional hybrid structures, P4. Polymer multifunctional sliding materials and P5. Fundamentals and modelling (FUNMODE). There are altogether 38 industrial companies and 7 research institutes participating in the HYBRIDS program. [21]

## 3.1 Multifunctional thin coatings (P1)

HYBRIDS program is a wide study of different disciplines as mentioned in the previous chapter. This master´s thesis is part of the P1 project which studies multifunctional thin coatings. In this project there are numerous of different industries and research institutes as partners. The participants in this project are listed as follows. Fiskars, LM-Instruments, Oras, Picodeon, Picosun, Ruukki Construction, SSAB Europe, Piikkio Works, Aalto University, Hämeenlinna University of Applied Sciences (HAMK), Tam-

pere University of Technology (TUT) and Technical Research Centre of Finland (VTT). [22]

P1 project divides into two separate subcategories which are metallic hybrids and polymeric hybrids. The main goal on both subcategories is to produce innovative surfaces with diverse multifunctionality. Different functions which to aim, are among others, long-term corrosion resistance, high durability, visual appearance, visual stability and specific friction characteristics. Cost effective and sustainable manufacturing technologies of both metallic and polymeric multilayer and multifunctional thin coatings are studied. [22]

In metallic hybrids the potential lies in functionally colored/dyed zinc with thermal spraying based techniques. Other goal is to investigate a novel sol-gel based colored passivation coating that prevents white rusting of the zinc layer of the hot dip galvanized steel. In polymeric hybrids the focus is on special customer needs such as clean, hygienic, anti-microbial, dirt repellent, fire retardant, improved energy efficiency and anti-icing surfaces with long term durability, sustainability and proper formability. Main priority is to bring in new application technologies to considerably increase the functionality of the aforementioned properties. [22]

In polymeric coatings the desired functionality is generally in the same layer of paint that has all the other basic components such as pigments and fillers. In this project the function/functions desired for the coating are applied in an individual coating layer. This method is an economically and technically sound way of producing the desired functionality to the coating. Separating the different functions into different layers of the coating system it is possible to increase the long-term durability of the product and the effect of the functionality. [22]

P1 project is categorized in six different tasks (T1-T6) which each focus on the different goals and objectives mentioned in the previous paragraphs. This thesis is part of the T2: Clean, hygienic, anti-ice and anti-microbial surfaces for large area industrial applications. [22]

### 3.1.1 Task 2 (T2)

This task focuses on the novel applications within the field of thin film coating technologies to further understand and study the multilayer and multifunctional coatings. T2 divides into four different sections, the first one focuses on the new thin film coating technologies i.e. SLIPS, sol-gel ($TiO_2$, $SiO_2$), ALD, siloxane and novel tubular coating applications by studying the coating itself, the surface treatment of fillers and other paint components. The second section focuses on spray coating by supercritical carbon dioxide ($ScCO_2$) as a solvent to attach surfactants and particles on polymeric coatings. Third section includes the objectives that are researched in this master´s thesis. In this

section the water-borne thin organic coating (TOC) substrate is studied as a basis for high durable base coat and functional clear lack top coat. Last section governs the encapsulating technology to provide controlled release of antimicrobial agents. [22]

This master´s thesis is part of the task 2 as mentioned previously. The aim of the thesis is to study and understand the interactions between the TOC layer and the first coating layer. In the experimental section of the thesis polyester, polyurethane and PVdF based binder systems are tested and analyzed to ultimately reach for the optimal coating layer on top of the TOC layer.

# 4. THIN ORGANIC COATINGS

The definition of TOC or thin organic coating varies slightly depending on the source. The factors that combine the definitions and ultimately classify a coating to be referred to as TOC are the following. TOC has an organic resin component, inorganic component for conductivity or corrosion resistance, and a dry film thickness of less than a few microns. Thin organic coatings have been around for tens of years, but started to resurface as a viable option for corrosion prevention in the recent years. History of thin organic coatings goes as far as the 1970´s, but the focus on this thesis is in the novel non-chromium thin organic coatings. The modern era for TOC started with the classification of hexavalent chromium as a carcinogenic substance in the 1990´s. The RoHS directive that was put to life in 2006 restricts the use of hexavalent chromium substances significantly. [23][24][25]

As a general rule in organic coatings, it could be considered that the thicker the film is the better the properties are. The composition, structure and conformation of the macromolecules at the substrate surface however differ from that of the bulk film. The thin layer adjacent to the substrate has different properties than rest of the coating. This adjacent layer governs the most important factor of organic coatings; the adhesion. The combination of inorganic materials and organic polymers gives the system a wide range of profitable properties. Inorganic nanoparticles bring out properties such as rigidity, high thermal stability, strength, hardness and corrosion resistance, whereas the organic polymer gives the system flexibility, ductility, and dielectric properties. Inorganic material (e.g. titanium) acts as a corrosion inhibitor via passive film formation, behaving in a similar way than the chromium predecessor. [26][27][28]

The reason for the growing interest in TOC based products lies on the environmental and economic standpoints. If an adequately good product without a pretreatment layer and a primer layer could be manufactured the coating process would simplify and therefore cost savings would appear. In Figure 4.1 is a comparison of a classic coil coating system and a novel TOC based coil coating system; also illustrated in the figure is the 3-layer coil coating system in both the classic and the novel way.

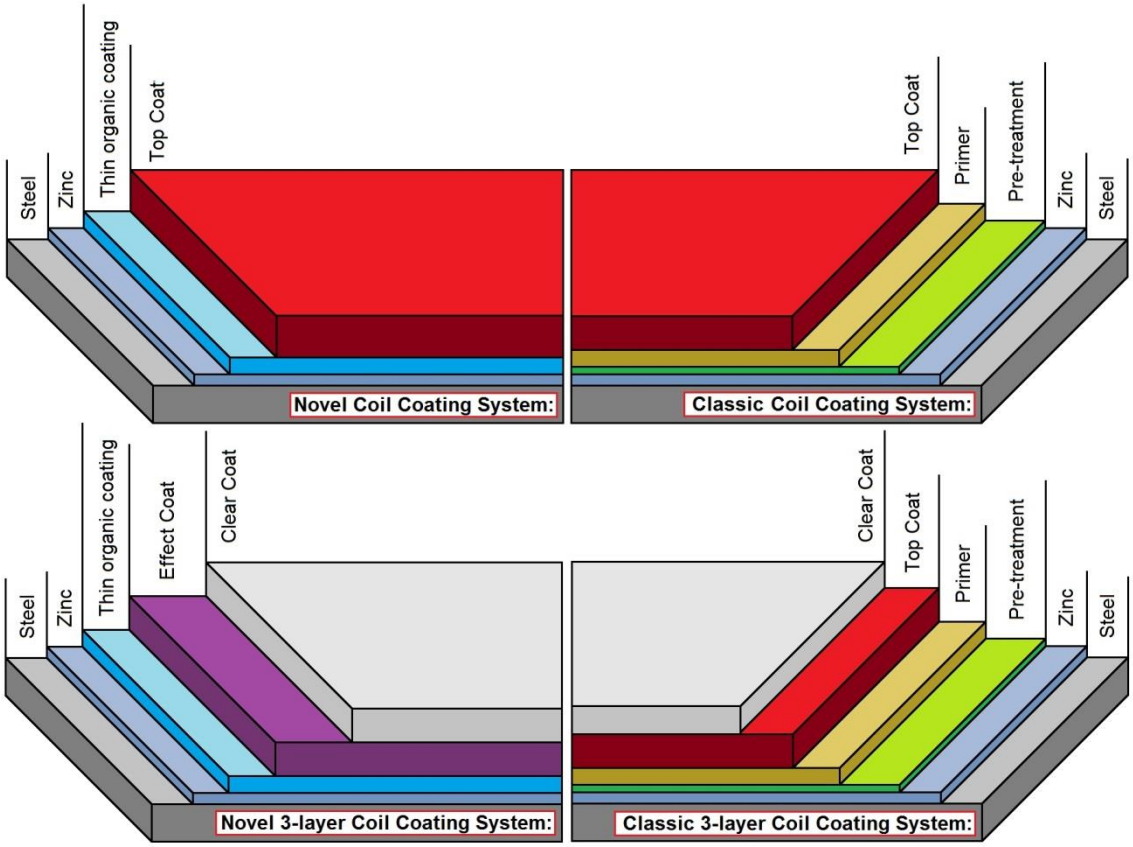


***Figure 4.1:*** *Illustration of the differences in TOC based coating systems and classic pretreatment + primer coating systems*

If the ideal coating process for the TOC could be arranged, discussed in the next subchapter 4.1 Optimal TOC application method in Hämeenlinna, the environmentally cumbering alkaline washing phases could be removed from the coil coating line. Cost savings from the reduced consumption of chemicals and water would be noticeable. When the transition to 100 % hexavalent chromium free production was made and the use of titanium pretreatment grew, a compromise from the excellent performance of the chromium products had to be made. This transition opened a way for the development of new substitutive methods, which bring adequate corrosion protection and simultaneously other good properties to the finished coating system. The transition and the growing interest on the novel TOC based products forced pretreatment manufacturers and paint manufacturers to race against each other on filling the new market segment. [27][28][29]

Chromium free TOCs have introduced themselves as one of the alternatives for the old chromating process. The TOC systems discussed and studied in this thesis are acrylic based aqueous solutions that are applied in the coil coating line. Former Ruukki Metals´ research and development projects have led to two different TOC options that are applied on hot dip galvanized (HDG) steels. In this chapter the reasons for the use, application of and the properties of thin organic coatings are discussed. In the subchapter 4.2

The selection of TOC 1 and TOC 2, the selection process of the two TOCs to be used in line trials and in this thesis are discussed in more detail. [23][24][25]

TOCs are already widely used in electronics, cars and home appliances by such large producers as Jaguar, Ford, Renault, Honda, Siemens, Miele and Bosch. In 2009 TOC based steel products saw about 50 % increase in use. Similar trend of increase was reported also in the year 2010 with 60 % increase in the use of the above mentioned products. In perspective of global steel markets, few of the biggest companies in the business have started to market TOC based products with trademark names such as AcryZinc® (US Steel), EasyFilm-E® (Arcelor-Mittal), DURGRIP® (Nippon Steel) and ReziBond® (The American Steelscape Company). Arcelor-Mittal alone has produced over 700,000 tons of EasyFilm-E based steel in the last several years. Although widely used in other fields of industry, the development and research of TOC based coating systems in coil coating lines are still relatively non-existing. [23][24][25]

The ultimate aim of TOC based coatings lies in the replacement of traditional pretreatment processes and even rendering the primer unnecessary. Without the need for the primer, an additional functional coating layer could be painted, resulting in a multilayer coating with new improved properties. In this thesis two separate thin organic coatings were selected for further studies. The above mentioned coating systems performed with the best results in earlier testing as explained later in the subchapter 4.2 The selection of TOC 1 and TOC 2. The thin organic coatings chosen for the thesis project and for further testing in coil coating line are explained with detail in the subchapters 4.3.1 TOC 1 and 4.3.2 TOC 2. [23][24][25]

## 4.1 Optimal TOC application method in Hämeenlinna

Although the vast history of the thin organic coatings in general, they are still a novel and quite experimental products in the coil coating industry. The utilization of TOC in Hämeenlinna is under research and therefore the optimal way of application is not yet readily available. In the experimental stage of the product development a number of compromises have to be made. If the research shows that the TOC is a viable option for coil coating a series of investments should be made to optimize the coating process. The optimal coating process is not addressed in this thesis with much detail, but a general idea of the optimal system is discussed.

As discussed in the previous chapter the TOCs for this thesis were applied in the line trials. The line trials were done in the coil coating line with the spray and squeeze system or with the primer coating system. If an optimal performance and economical application method is used, the TOC is applied right after the hot-dip-galvanization process. The preferred way to apply thin organic coatings is with a non-rinse technology, roll coater and drying. The roll coater system that would ideally be used after the galvaniza-

tion is similar to the roll coater used to apply the primer coating layer in the coil coating line (2.1.1 Coil coating line in Hämeenlinna). The curing of the TOC should be done with a significantly lower PMT than with primer coating layer. The preferable PMT would be approximately 80 °C. [30]

The main advantage, if the TOC is applied immediately after the hot-dip-galvanization process, is that the whole coil coating line can be used to apply coating layers with specific functionality. With the coil coating line that is used in Hämeenlinna, there are two separate roll coater units, one for the primer and one for the top coat. The ultimate goal of the TOC research is to render the pretreatment process and primer coating layer unnecessary, simultaneously opening a possibility to apply multilayer coatings without the need to run the coil two separate times through the coil coating line. Without the second run through the coil coating line significant saving could be made and the multilayer coating could possibly become a more profitable product.

Hot-dip-galvanized steels need to be protected against white rusting and other corrosion phenomena. Traditionally oil is used to seal the surface of the coil and therefore hinder the corrosion media from reaching the surface of the coil. TOC based products are already used to protect HDG steel from such corrosion, removing the oiling phase, but these TOC products are not that suitable for coil coating processes. Development for a TOC product (for example TOC 1 and TOC 2) that could be readily coil coated and performed adequately as a replacement for traditional pretreatment and primer is ongoing. In addition to rendering primer and traditional pretreatment unnecessary, the alkaline wash cycles in the coil coating line could be removed. [28][29]

Multilayer coating can open a possibility for the manufacture of functional coatings. Functionalities that are associated with multilayer coatings are among others, self-repairing, self-cleaning and antimicrobial surfaces. Single or double layer clear coats are also a possible way to benefit from multilayer coatings. With reasonably inexpensive base coating for the basic properties and with a clear coat layers for additional properties and protection more economical coating could be manufactured.

Although not readily available, the optimal TOC coating method discussed above is theoretically already possible in the Hämeenlinna factory. In one of the galvanizing lines, a roll coater system is already in use. If the TOC appears to be a viable option for the traditional coating system, with a reasonable modification the possibility for the optimal coating process could be achieved. Although the roll coater system is already in place at one of the galvanizing lines, it would force all the TOC products to go through just that specific line and complicate the process of other metal coated products. Optimally the roll coater systems should be placed after each of the galvanizing lines to make it possible and effortless for each of the lines to produce TOC products for the coil coating line.

## 4.2 The selection of TOC 1 and TOC 2

Thin organic coatings have been around for a long time. However with the new interest in the TOC behavior and performance as a pretreatment primer, a long term research project has been launched. The former Ruukki Metals has tested different TOCs in a laboratory scale during the past years. The results from the tests in the past and with a mapping of the current situation of TOC manufacturers, a project concerning TOCs started in 2010.

In the first half of 2011 a group of different TOC manufacturers were approached and a steel sheet with their current TOC product was ordered. In the beginning of the project altogether seven different manufactures were considered; the manufacturers were as follows. AD-international (CCT), Valspar, Henkel, BASF, Chemetall, ProCoat and Beckers. The painting and testing of the first test set was done in the second half of 2011. Throughout the whole research project Ruukki Metals worked closely with Top Analytica and most of the TOCs and paints were applied by Top Analytica. After the first test series the TOCs with best performances were selected. New test series were administered to the remaining TOCs and after the conclusions from the latest test results the potential TOC list narrowed even further. Through 2012 and 2013 test sets 2 and 3 finalized the list of potential TOCs to be TOC 1 and TOC 2.

### 4.2.1 Test results for the chosen TOCs

Impact resistance, T-bend, T-bend + QCT 60 °C (48h) and the humidity test in 40 °C and 60 °C were administered to each of the potential TOC systems. The impact resistance test and T-bend test show similar results throughout the series for all of the tested TOCs. Humidity tests QCT 40 °C (1500 h) and QCT 60 °C (1000 h) were the conclusive tests that showed the superior performance of the TOC 1 and TOC 2 compared to the rest of the tested TOCs. TOC 1 and TOC 2 were practically unaffected by the humidity tests, other TOCs showed significant damage from the test cycles. TOC 1 and TOC 2 came out of the QCT tests with a result of 0 (best) the other TOC samples suffered damage up to 4s2 and 3s3. [31]

Notable for both TOC 1 and TOC 2 is the higher SFE (Surface free energy) compared to other TOCs. Simultaneously the contact angle with water is much lower in case of the two TOCs selected for further testing. Both of the above mentioned properties are linked to better wetting and therefore to better adhesion properties between the coating layers. Surface energy and contact angle measurements were done by Ville Saarimaa from Top Analytica. [31]

More detailed information about surface energy, contact angles and adhesion is found from chapter 5.1 Structure of the paint. Detailed information about the test methods and

explanation of the typical results for impact resistance, T-bend and humidity resistance is found in chapter 6.4 Testing methods. The same test methods were used in this thesis as a way to study the adhesion and overall performance of the first coating layer on top of the two previously mentioned TOC systems.

## 4.3 TOC 1 and TOC 2

The two chosen thin organic coatings are slightly different in composition and were therefore treated and applied differently. The first thin organic coating (TOC 1) that was coated at line trials is considered to be similar with the traditional pretreatment. The other thin organic coating (TOC 2) resembles more of the primer layer of the traditional system. TOC 1 was applied in the line trial with the spray and squeeze system described in chapter 2.1.1 Coil coating line in Hämeenlinna. TOC 2 was applied with the primer machine described in chapter 2.1.1 Coil coating line in Hämeenlinna.

### 4.3.1 TOC 1

The manufacturer of TOC 1 has a wide variety of thin organic coatings available, some of which are made with hexavalent chromium (VI), some with trivalent chromium (III) and some without chromium (TOC 1). Due to the transition to a fully chromium-free coil coating process, the chromium free version was preferred. TOC 1 is a waterborne acrylic conversion coating in the gauge range of a few tens of nanometers with a dry film weight of approximately 1-2 g / $m^2$. [32]

Laboratory painted samples of the TOC 1 were tested and evaluated against traditionally coated reference samples and trivalent chromium TOC samples of the same manufacturer. All TOC systems were finished with Purex top coats; with traditional pretreatment and also a primer layer was used. In Table 4.1 the results for the TOC 1 compared to TOC 2 and reference samples can be observed. The results show that the chromium free version (sample number 1) is comparable to the other options (sample numbers 2-8). [32][33]

***Table 4.1.*** *Impact resistance, T-bend and T-bend + QCT 60°C test results for TOC 1 and TOC 2 compared to the traditional systems (modified) [32][34]*

| Sample number | THIN ORGANIC COATING Reference sample | Coating (Color) | Thickness [µm] | Impact resistance (Adhesion) [lbf in] | T-bend (adhesion) [T] | Visually evaluated after the test. The scale: from 0 (no defects) to 4 (severe cracking) | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | 0 T | 0.5 T | 1 T |
| 1 | TOC 1 | Purex (Black) | 18 | 160 (160) | 0.4 (0) | 3.0 | 3.0 | 1.0 |
| 2 | TOC 2 | Purex (Black) | 18 | 160 (160) | 0.6 (0) | 3.0 | 3.0 | 1.0 |
| 3 | Reference (Cr-free) | Purex (Black) | 24 | 160 (160) | 0.0 (0) | 2.5 | 2.5 | 0.0 |
| 4 | Reference (Cr-free) | Purex (Red) | 24 | 160 (160) | 0.2 (0) | 3.0 | 2.5 | 1.0 |
| 5 | Reference (Cr-free) | Purex (White) | 27 | 160 (160) | 0.7 (0) | 3.0 | 2.5 | 1.0 |
| 6 | Reference (Cr-free) | Primer + Purex (Black) | 24 | 160 (160) | 0.0 (0) | 2.5 | 2.5 | 0.0 |
| 7 | Reference (Cr-free) | Primer + Purex (Red) | 24 | 160 (160) | 0.2 (0) | 3.0 | 2.5 | 1.0 |
| 8 | Reference (Cr-free) | Primer + Purex (White) | 27 | 160 (160) | 0.7 (0) | 3.0 | 2.5 | 1.0 |

Mechanical properties were not affected with the change from the traditional pretreatment and primer system to the chromium-free TOC as seen in Table 4.1. Similar results were obtained from QCT tests in 40 °C and 60 °C. QCT tests show that the humidity resistance is in the same range as with traditional pretreatment with a score of 0 (best). TOC 1 was chosen for line trials and to be used as one of the TOCs in the experimental phase of this thesis. [32]

The structure of the TOC 1 with white Purex top coat is shown in Figure 4.2. As can be seen, the thin organic coating layer is comparable in thickness to a traditional pretreatment.

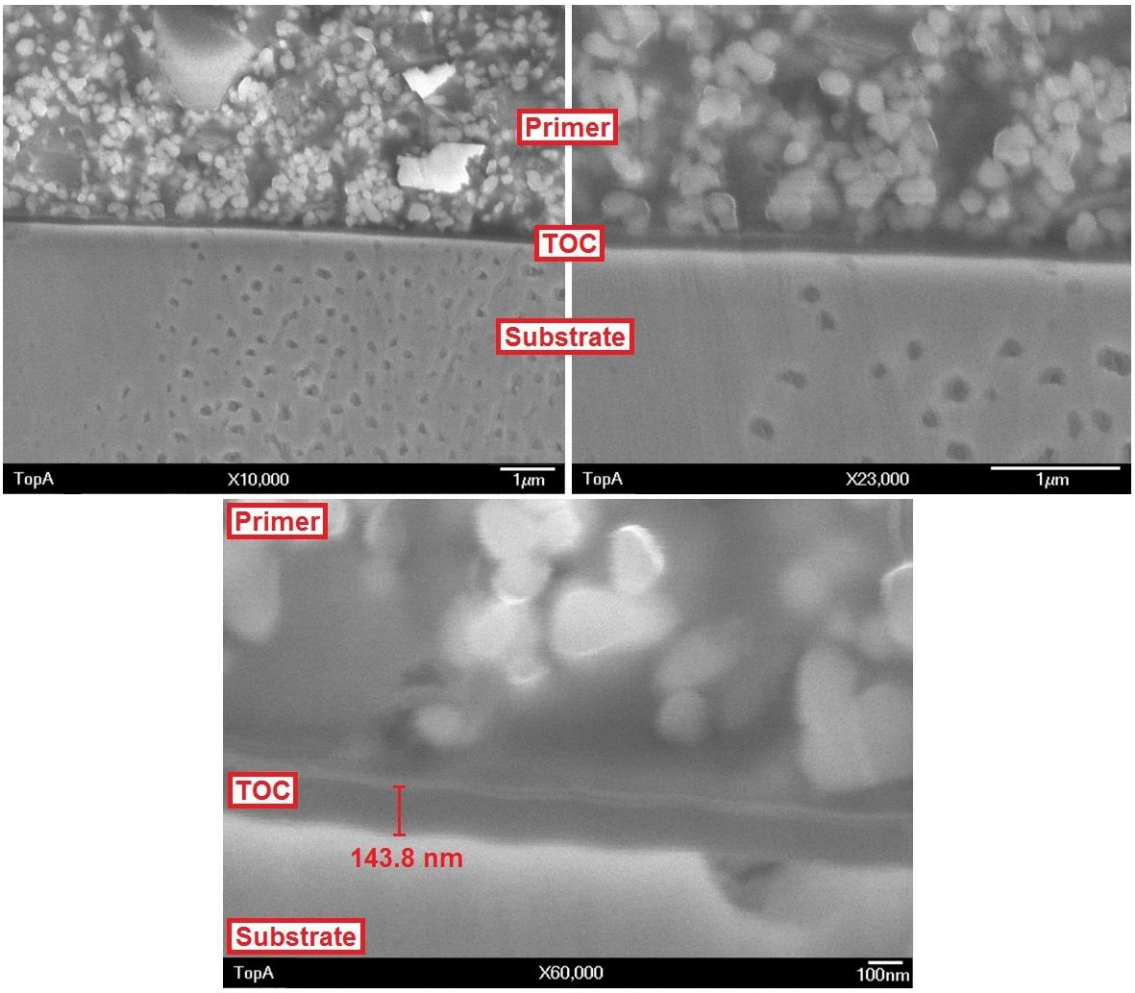


***Figure 4.2.*** *SEM image of the TOC 1 + Primer coating system (modified) [31]*

Further discussion of the line trial and the properties of the TOC 1 can be found from the experimental part of the thesis in subchapter 6.1.1 TOC 1 line trial.

### 4.3.2 TOC 2

The manufacturer of TOC 2 also offers TOC products with trivalent and hexavalent chromium, again in accordance with the transition to chromium free coil coating lines the chromium free (TOC 2) version was preferred. TOC 2 is a water borne product and it is free of volatile organic compounds (VOCs). The thin organic coating is formed from an acrylic water-borne solution with a pH of 10.5. The coating is colored with inorganic white pigments for optimal opacity. The gauge of the TOC 2 coating is in the range of 1-3 µm. [34]

Laboratory samples of the TOC 2 (sample number 2) were compared against traditionally pretreated line samples (sample numbers 3-8). As can be seen from Table 4.1, similar results were obtained with the new TOC 2 coating as a pretreatment primer compared to the traditional pretreatment and primer combination. All samples were coated with Pu-

rex top coat and tested with the same standard testing methods for coil coated products as TOC 1.

Mechanical properties and humidity resistance were both excellent and TOC 2 was selected for line trials. TOC 2 is the second base for the samples prepared for the experimental part of this thesis. The structure of the TOC 2 with black Purex as a top coat can be seen from the scanning electron microscope (SEM) image in Figure 4.3. Notable difference between the two TOCs is the thickness of the coating. TOC 2 is in the range of a few microns in thickness, whereas TOC 1 is in the range of few tens of nanometers thick. [34]

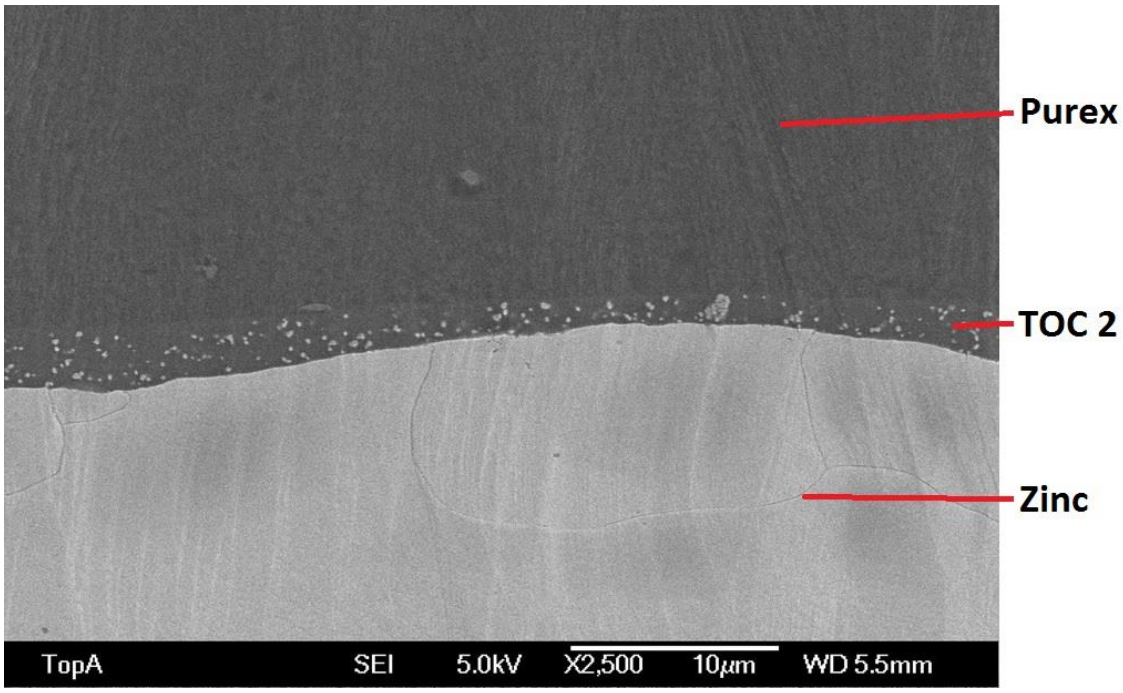


***Figure 4.3.*** *SEM image of the TOC 2 + black Purex coating system (modified) [34]*

Further discussion of the line trial and the properties of the TOC 2 can be found from the experimental part of the thesis in subchapter 6.1.2. TOC 2 line trial.

# 5. STRUCTURE OF THE PAINT AND DIFFERENT BINDERS

Paint is the liquid version of the final coating before it undergoes the curing process where the solvents evaporate and the crosslinking of the polymer binder occurs. The final properties of the coating are dependent on the structure and ingredients of the paint and the suitability of the paint for the process parameters. Two of the most vital factors in continuous coil coating are the applicability of the paint and the required properties of the dry film. Continuous coating of the steel coil with organic paint requires a suitable rheology, adequate wetting behavior and film formation of the paint. Final properties of the coating include UV-radiation resistance, corrosion resistance, appearance and other mechanical and chemical properties. All of the properties mentioned above are fabricated with the combination of the chemistry of the paint and the painting process. [3][4]

The purpose of the paint is to adhere to its substrate, being either the previous coating layer or the steel substrate, and to form a protective film on the surface. The paint must dry within a relatively short period of time due to the 25-35 second interval in the convection oven. To achieve the requirements mentioned above, the constituents of the paint must be carefully selected. In this thesis a number of different combinations of polyester, polyurethane and polyvinylidene fluoride based paint systems are applied on the surface of the thin organic coatings chosen for this thesis. The purpose is to find out which of the selected binders are most suitable for the different TOCs mentioned in subchapter 4.3 TOC 1 and TOC 2. [3][13]

## 5.1 Structure of the paint

Paints can be roughly presented as the combination of four different elements. The main elements in all paints are as follows, the solvent (i.e. carrier media), binder (i.e. resin), pigments and other additives. Functions of different ingredients are discussed in this chapter, paying closer attention to the binders used in the experimental part of the thesis. The basic principles of rheology and surface chemistry are needed to understand the process of paint application. Rheology describes the science behind the flow of the liquid paint and surface chemistry governs the science behind the wetting of the surface. These two separate subjects, as well as the glass transition temperature and adhesion are discussed in the following subchapters. [4][34]

### 5.1.1 Rheology

The most important aspect of rheology in coating applications is viscosity. The viscosity of the paint is of vital importance in order to apply the paint via roll system and to successfully wet the surface of the substrate with a uniform layer of paint. Viscosity **η** [Pa x s] describes the ability of the paint to resist flow i.e. the ratio of shear stress **τ** [$Ncm^{-2}$] to shear rate **D** [$s^{-1}$]. [3]

Viscosity can be defined with the ratio described above. The shear stress is a ratio of forces **F** [N] to area **A** [$cm^2$] in which the forces are applied. Illustration of the stationary situation, before the paint is influenced by forces of the rolls, can be seen in Figure 5.1.

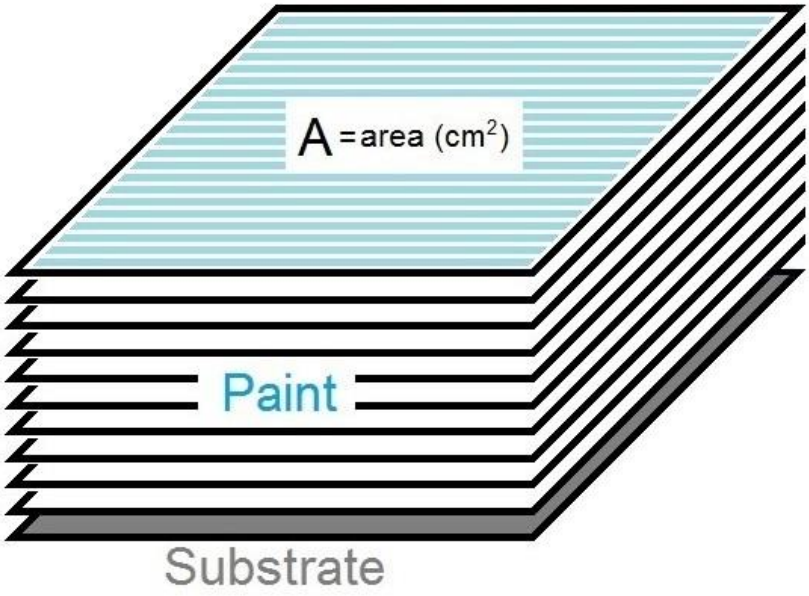


***Figure 5.1.*** *The structure of the paint between a stationary surface (substrate) and moving surface (rolls) before force is applied (modified) [36]*

When the rolls rotate and apply pressure to the surface of the paint, the top layers of the paint, adjacent to the moving surface, move faster than the ones adjacent to the stationary surface. The above described situation creates forces known as shear stresses. The shear rate is described as the ratio of velocity **v** [$cms^{-1}$] of which the forces affect to thickness **l** [cm] of the paint film. Illustration of the paint film when applied with the forces and velocity of the rolls is shown in Figure 5.2. All the necessary variables needed to describe the viscosity of the paint are illustrated in Figure 5.2.

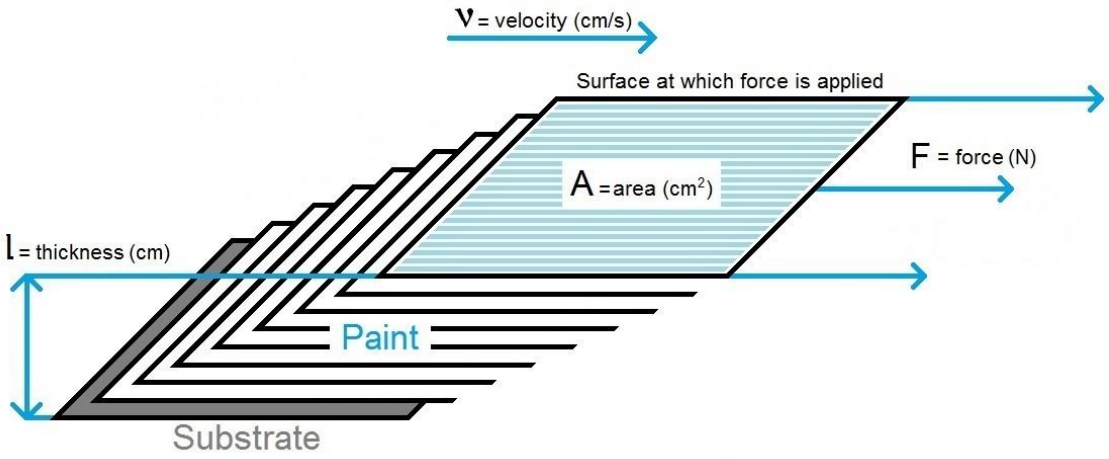


***Figure 5.2.*** *The structure of the paint between a stationary surface (substrate) and moving surface (rolls) when applied with forces of the rolls (modified) [36]*

Paints are described as non-Newtonian fluids which means that the viscosity of the paint changes significantly when influenced by outside forces. The higher the viscosity is, the higher the resistance towards the flow is. During coil coating process the paint is a subject to outside forces of the rolls, mixers etc. The speed and nip pressure of the rolls lower the viscosity of the paint and therefore the process parameters must be carefully monitored. [3][35][36][37]

Most paints act with **pseudoplastic** behavior where the increase of shear rate (i.e. roll speeds) lower the viscosity of the paint. This phenomenon is called shear thinning. When the outside forces are removed the viscosity of the paint returns to normal with a delay, which greatly helps to achieve a uniform spread of the paint layers. The delayed return to the normal values of the viscosity is called **thixotropy**. Thixotropic behavior and the shear thinning of the paint are shown in Figure 5.3.

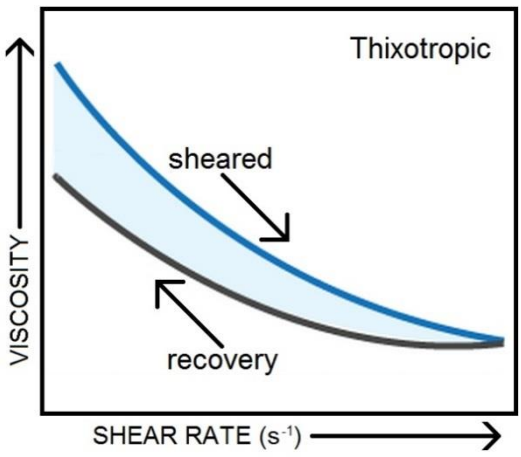


***Figure 5.3.*** *Illustration of thixotropic behavior*

Binder, pigments and other additives affect viscosity in a specific way, usually the addition of said ingredients increase the viscosity of the paint. Increase in temperature lowers the viscosity of the paint. Mostly though, viscosity of the paint system is controlled with the use of correct solvent and with the right amount of the said solvent. Viscosity is one of the factors that govern the thickness of the painted layer and affects the quality, appearance and homogeneousness of the coating layer. Controlling the viscosity of the paint is of utmost importance when good quality products are manufactured. If the viscosity is too low a selection of the following could happen. Uneven color, stripes, changes of color, cracks, spots, gauge variations of the paint film, visible edges of the paint, sagging and stratification of the pigments. On the other hand if the viscosity is too high it will result to the following problems. The leveling of the paint will be poor, there might appear pinholes in the structure, imprints of the rolls could be visible or the surface of the paint could remain wrinkled. [3][35][36][37]

### 5.1.2 Surface chemistry

Surface chemistry is a field of science that deals with the interface of two materials. In the coating applications the interface can be simplified as being the interface between the liquid paint and the solid substrate material. One of the factors that is really important when concerning the coatings wetting ability and the ability to adhere to the surface is the surface tension.

Surface tension **T** [dyn/cm, $mJ/m^2$] refers to the force per unit length needed to break the surface of the liquid. The cohesive forces between the molecules in the liquid are responsible for surface tension. When close to a similar neighboring atom, attractive forces between the atoms are exerted. With the interface between the air and the paint film, there are no similar molecules on the air than on the surface of the paint. This leads to stronger attraction forces between the molecules on the surface and to the molecules just under the film surface. This attraction between the surface molecules and molecules just under the surface is a phenomenon called surface tension. The attractions between the molecules in the paint film are illustrated in Figure 5.4.

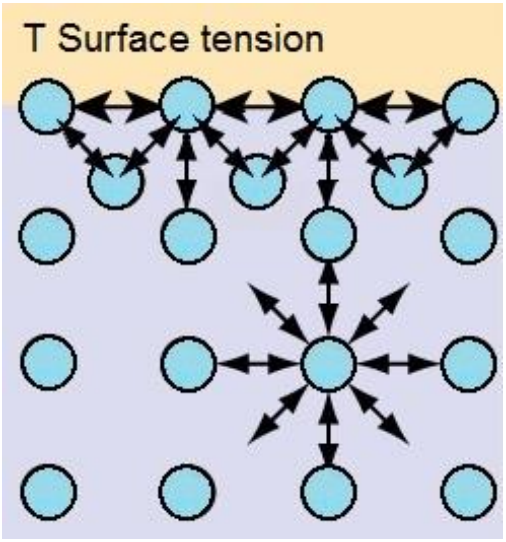


***Figure 5.4.*** *Illustration of the intermolecular forces between the molecules in the surface of a paint film (modified) [38]*

These above mentioned intermolecular attractive forces are also exerted towards the solid substrate material, therefore contributing to the wetting and adhesion of the paint. The attraction between the solid substrate material and the liquid paint is discussed with more detail in subchapter 5.1.4 Adhesion. [3][35][38]

The wetting ability of the paint is closely related to its surface tension and to the surface (free) energy **SFE** [dyn/cm, $mJ/m^2$] of the substrate. Proper wetting happens when the paint can penetrate the ridges and the crevices of the surface roughness and spread uniformly on the surface. If the surface tension of the paint is smaller than the surface energy of the substrate an adequate wetting and therefore good adhesion is possible. The codependency between these properties can be estimated with Young's equation. [3][35][38]

The contact angle of the paint must be small enough for the paint to spread on the surface. If the contact angle $\theta > 90°$ (Figure 5.5. a) the substrate and the paint repels each other and a proper wetting is impossible to obtain. When the contact angle $\theta < 90°$ (Figure 5.5. b) the paint wets the surface of the substrate quite well and a good level of wetting is achieved. The ideal wetting is achieved when the contact angle $\theta << 90°$ (Figure 5.5. c), if the contact angle can be dropped to 0° a complete wetting of the surface is achieved.

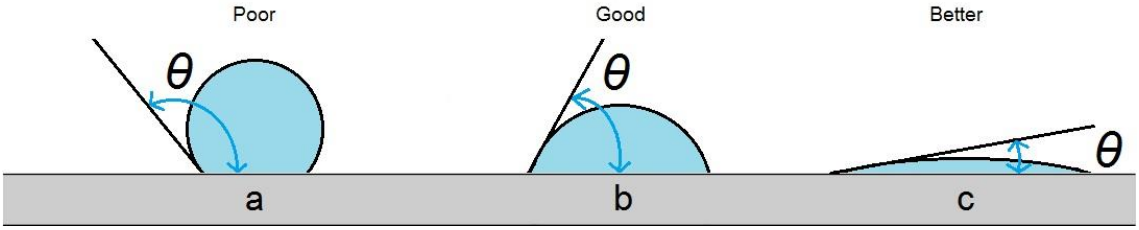


***Figure 5.5.*** *Different contact angles for the paint (modified) [35]*

Surface energies of the substrate materials are usually quite low, especially the coating layers that are to be painted over with additional layers of paint. In order to achieve proper wetting, additives are used to lower the paints surface tension. **Surfactants** (i.e. wetting agents) are said additives that lower the surface tension of the paint. Surfactants have two different chemical groups, one that associates with the binder and one that has a lower surface tension than the binder itself. The group that has lower surface tension makes the coating behave as if it has the lower surface tension, therefore wetting the desired surface. Surfactants can also lower the surface energy of the finished coating, therefore making it harder for the subsequent layer of the coating system to adhere. [3][4][35]

### 5.1.3 Glass transition temperature

Glass transition temperature (**$T_g$**) is described as the temperature below which an amorphous polymer is in a hardened and brittle (glasslike) state. Above the $T_g$ amorphous polymers are in a soft and flexible (rubberlike) state. With crystalline polymers similar behavior is not observed, rather a crystalline melting point **$T_m$** is found. Above the $T_m$ the crystalline polymer is in a form of a viscous liquid with some elastic response or as a liquid. Below $T_m$ there can be seen two different regions, either a glassy matrix with crystallites or a rubbery matrix with crystallites. Usually polymers that are used in coating applications are partly amorphous and partly crystalline. With semi-crystalline polymers the glass transition phenomena happens in the amorphous phase, while the crystalline phase remains unaltered until the $T_m$ is reached, after which the crystalline structure starts to melt. In the Figure 5.6 concept of glass transition and crystalline melting is illustrated with the specific volume of the polymer in relation to the temperature increase. All six of the above mentioned phases with semi-crystalline polymers are represented in the Figure 5.6 with letters from A to E. [3][39][40]

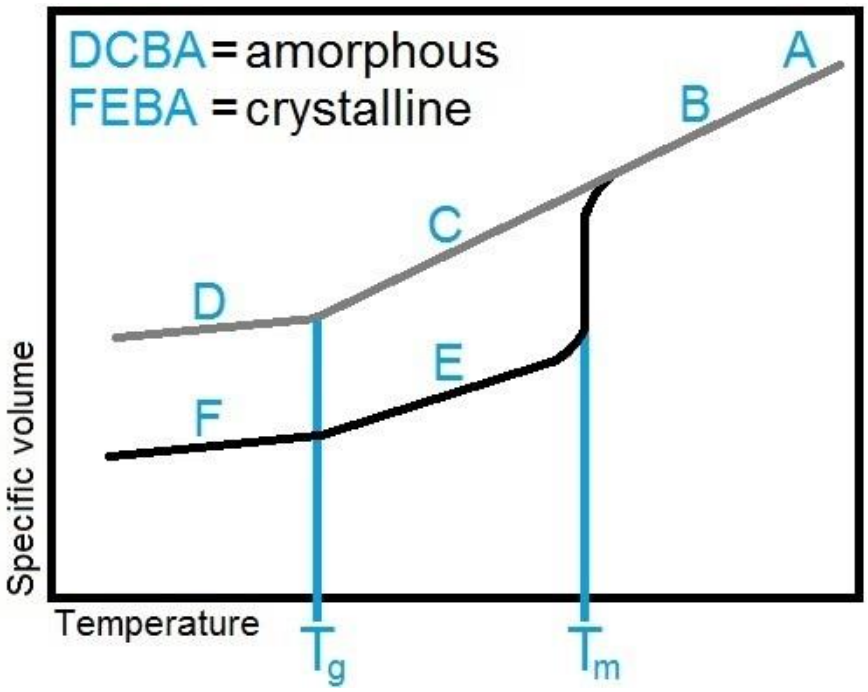


***Figure 5.6.*** *Specific volume - temperature curves for a semi-crystalline polymer. (A) Liquid region; (B) viscous liquid with some elastic response; (C) rubbery region; (D) glassy region; (E) crystallites in a rubbery matrix; (F) crystallites in a glassy matrix (modified) [39]*

Many of the properties of the finished coating are in correlation with the glass transition temperature of the polymer. Solution viscosity, solvent release, drying speed, adhesion, hardness, impact resistance, toughness, tensile strength, and abrasion resistance among others are influenced by the glass transition temperature. This variable is unique to the polymer used as a binder, but is altered when the symmetry, chain stiffness, intermolecular forces, the molecular weight distribution changes. The amount of plasticizers, the level and type of pigmentation and the degree of crosslinking also impact the glass transition temperature. [40]

### 5.1.4 Adhesion

Adhesion is the most vital attribute that the protective coating has. Other properties, no matter how remarkable, are quite useless if the coating does not possess adequate adhesion to the substrate. The protection against humidity and corrosion is linked closely to the ability of the coating to stick to the underlying material. Adhesion can be defined by different theories, which are mechanical bonding, chemical bonding and physical bonding (absorption, electrostatic attraction). With coatings that possess good adhesion, usually a combination of the above mentioned mechanisms are involved. [35][41]

In addition to adhesion, cohesion plays an important role in the durability of the coating. Cohesion is the inner strength of the material determined by the intermolecular forces in the bulk. A good cohesion in the coating layer ensures that the coating itself will not

rupture or crack. In order for a fracture to occur, outside forces must exceed the limit of the strength of cohesion/adhesion bonds. In a rather simplified manner when subject to outside forces, if the cohesion is greater than the adhesion, an adhesion failure will occur, and vice versa. In Figure 5.7 the main difference between adhesion and cohesion forces are demonstrated. The colored lines represent the mechanisms of adhesion and cohesion. If the fracture happens within a coating layer (red lines) it will be categorized as a cohesion failure. On the other hand, if the fracture happens in the interface of two separate layers (blue lines) it will be categorized as an adhesion failure. The adhesion forces in Figure 5.7 are considered to represent any of the above mentioned mechanisms. [13][35][41]

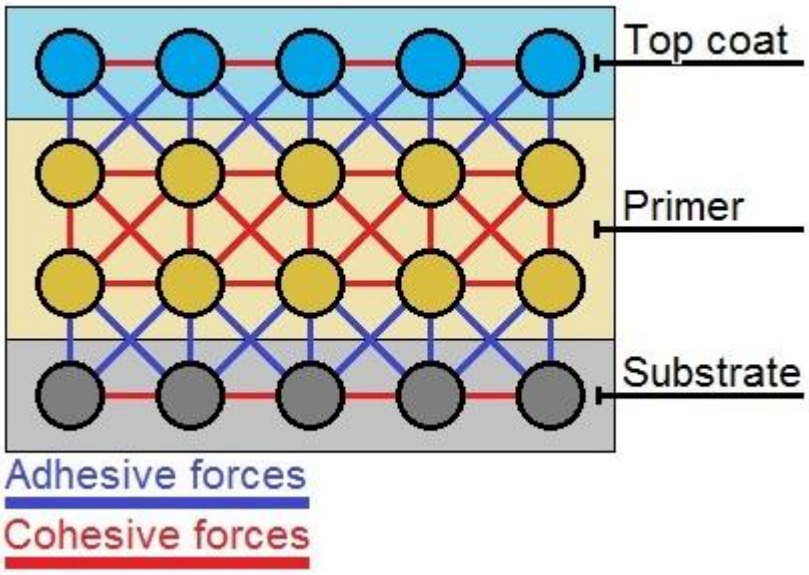


***Figure 5.7.*** *Adhesion forces and cohesion forces demonstrated in a system with substrate, primer and top coat*

**Mechanical bonding** represents the bonding mechanism of the coating to the pores, crevices, ridges, voids, holes and other types of surface roughness on the substrate (or the underlying layer of coating). The viscosity and the surface tension of the paint determine if the roughness of the substrates can be fully penetrated and a mechanical bond created after the curing of the coating. Mechanical bonding (i.e. mechanical interlocking) is the predominant mean of adhesion and the effect of a proper wetting of the surface is crucial. The surface of a substrate material (or the underlying coating layer) is never completely smooth. In the microscopic scale the surface is covered with ridges, peaks and valleys which increase the actual contact area of the substrate. When the paint displaces the air in aforementioned surface irregularities, it will interlock with the surface and crate a mechanical bond in the interface of the two different layers. Illustration of the mechanical bond is shown in Figure 5.8.

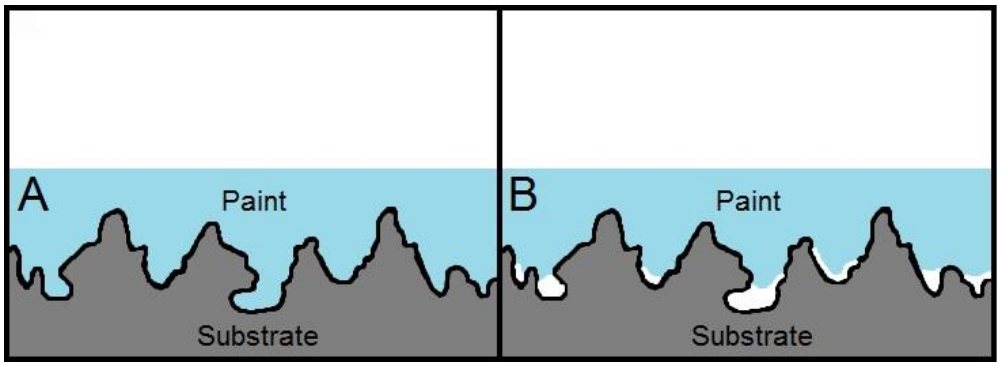


***Figure 5.8.*** *Illustration of the surface irregularities and the mechanical bonding of the paint, (A) Complete wetting; (B) Improper wetting with air bubbles on the substrates surface*

If proper wetting is not achieved, air bubbles will remain on the interface of the substrate and the paint. Air bubbles in the coating structure allow an accumulation of moisture in to the voids eventually resulting in a loss of adhesion. Mechanical adhesion and interlocking sites can be promoted to the system with the use of structured or textured finishes on the primer. With an increase of the amount of pigments above the critical pigment volume concentration (CPVC) mechanical bonding can be enhanced due to the newly obtained irregularities in the surface topography. [3][13][35][41][42]

**Chemical bonding** is a strong connection between the substrate and the coating across the interface via ionic, covalent or hydrogen bonds. In order for the chemical bonds to occur a mutually reactive chemical groups have to be present in the substrate and the coating. Certain paint systems have a functional group formulated within the binder to react with the substrate material. Adhesion promoters (i.e. coupling agents) are an additive which will form a molecular bridge across the interface of the paint and the substrate. Adhesion promoters have two separate functional groups, other to react with the binder of the paint and other to react with the substrate. Illustration of said molecular bridge is shown in Figure 5.9.

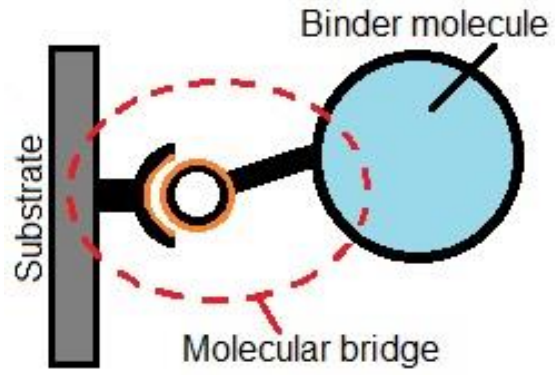


***Figure 5.9.*** *Illustration of a molecular bridge created with adhesion promoters between the binder molecule and the substrate (modified) [41]*

Organosilane is a widely used adhesion promoter in the paint industry. As an additive to the paint formula it improves the adhesion and therefore simultaneously improves moisture resistance and corrosion properties of the finished coating. As with all adhesion mechanisms also chemical bonding can occur only if a proper wetting is achieved and the distance between the paint and the surface is practically nil. [3][35][41][42]

**Physical bonding** is considered to include both absorption and electrostatic attraction mechanisms of adhesion. This theory states that the interface of the coating/substrate system has weak attractive forces. Secondary forces (van der Waals forces), dipolar interactions, hydrogen bonding and other low energy bonds are detected in the interface as shown in Figure 5.10.

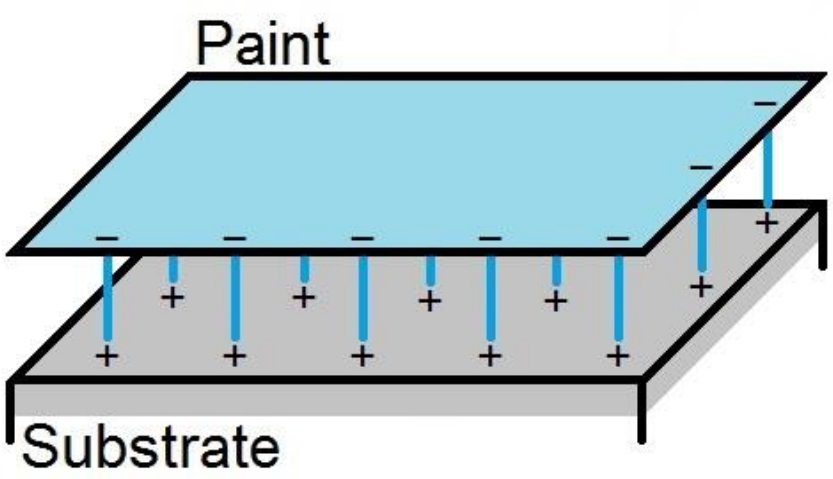


***Figure 5.10.*** *Illustration of weak secondary forces across the substrate/coating interface (modified) [42]*

Absorption theory states that intermolecular forces can be found in the interface only if the wetting of the substrate is adequate. When the wetting is adequate and the contact of the paint with the substrate is intimate, molecular contact between the two materials creates the above mentioned intermolecular surface forces. Electrostatic attraction between the substrate material and the surface coating is the other half of the physical bonding theory. Electrical double layer can be detected at the coating/substrate interface due to electrical charges spread throughout the system. [3][35][41][42]

## 5.2 Solvent

Paints in coil coating applications are in a liquid form. The liquid form of the paint is achieved with a **solvent mixture** that dissolves and disentangles the polymer molecules. The solvent also controls the viscosity of the paint for proper wetting properties and for the ease of application. Coil coating paints are dominantly solvent-borne, but the interests in waterborne paints are rising due to the shifting focus on the environmental issues of the solvents. Solvents are either pure or mixed liquids that do not chemically change

the material that they dissolve. When choosing a solvent mixture it needs to have similar properties than the substance (i.e. binder) to be dissolved. Solvents introduce repulsive forces between the components of the paint to avoid clustering and premature chemical reactions and to enable homogeneous distribution of the ingredients. As with everything else, the price, safety and the required properties of the final product governs the choice of the solvent mixture. Organic solvents such as alcohols, ketones, ethers, esters, aliphatic hydrocarbons and aromatic hydrocarbons are used. [3][37][43]

The solvent must evaporate fairly quickly during the curing process in the convection oven. The mixture of different solvents, with different evaporation rates, ensures that the coating cures evenly starting from the layers adjacent to the substrate towards the layers adjacent to the surface. Solvent mixture is not a part of the dry film and must therefore evaporate fully during the stay in the convection oven. Any unevaporated solvents significantly weaken the coating structure and can cause unwanted bubbles to the structure. In the experimental part of this thesis polyester, polyurethane and PVdF based paint systems are solvent-borne, unlike the TOCs used, which are waterborne. [3]

## 5.3 Binder

Binders are the main component of the cured dry film and therefore are mostly responsible for the properties of the final product. Binders form the matrix of the coating holding all the other components (e.g. pigments, additives). Binder adheres to the substrate and affects the adhesion properties significantly; therefore the choice of the binder plays the most important role when selecting a coating to specific environments.

Binders are divided into two separate categories; chemically cured and physically cured. In the chemically cured coatings a web-like structure of the coating is formed via polycondensation or polyaddition reactions after the evaporation of the solvents. With the physically cured products, the formation of the binder matrix happens without chemical reactions due to the evaporation of the solvents. In this thesis polyesters and polyurethanes are chemically cured whereas the waterborne TOCs and PVdF are physically cured. [3][4][37][43]

### 5.3.1 Polyester

Polyesters are a versatile coating option that are quite affordable and therefore the most used coating in the coil coating industry. Polyesters are binders that are manufactured with polycondensation reaction between dicarboxyl acids and dialcohols. Most commonly used diacids are the aromatic dicarboxyl acids (e.g. isophtalic acid, terephtalic acid) or aliphatic dicarboxyl acids (e.g. adipic acid) shown in Figure 5.11. [4]

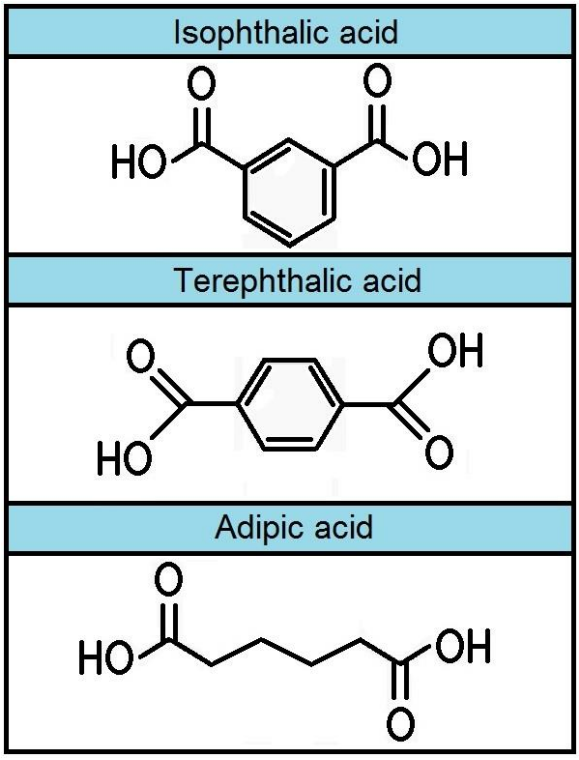


***Figure 5.11.*** *Most commonly used dicarboxyl acids in polyester manufacturing (modified) [3]*

With the proportions of the aromatic and aliphatic acids the $T_g$ (glass transition temperature) can be altered. $T_g$ ultimately affects the operating temperature properties of the finished dry film. Price of the ingredients and the desired service environment governs the choice of the diacid system. The diols used are selected based on price and required properties. The most used diols are diethylene glycol, 1,3-propanediol and 1,4-butanediol, shown in Figure 5.12.

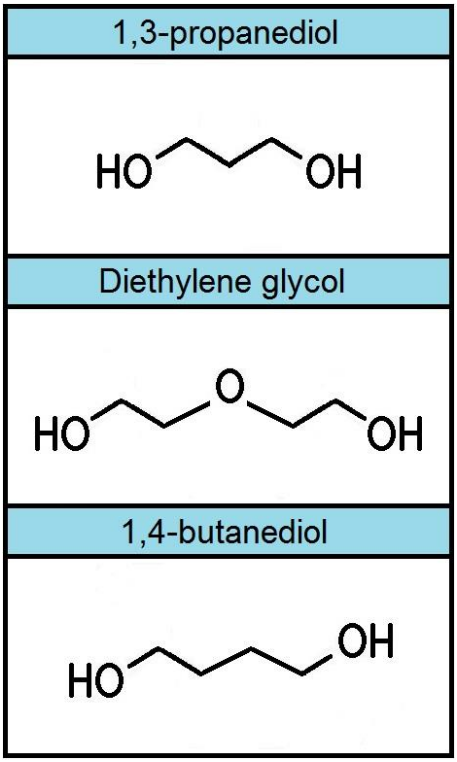


***Figure 5.12.*** *Most commonly used dialcohols in polyester manufacturing (modified) [3]*

If triols (e.g. trimethylol propane) are used, branching increases the number of hydroxyl groups per molecule and increases the resilience of the polymer. The basic reaction between dicarboxyl acid and dialcohol is shown in the Figure 5.13, where the colored blank boxes represent any group of atoms depending on the reactive dicarboxyl acids and dialcohols.

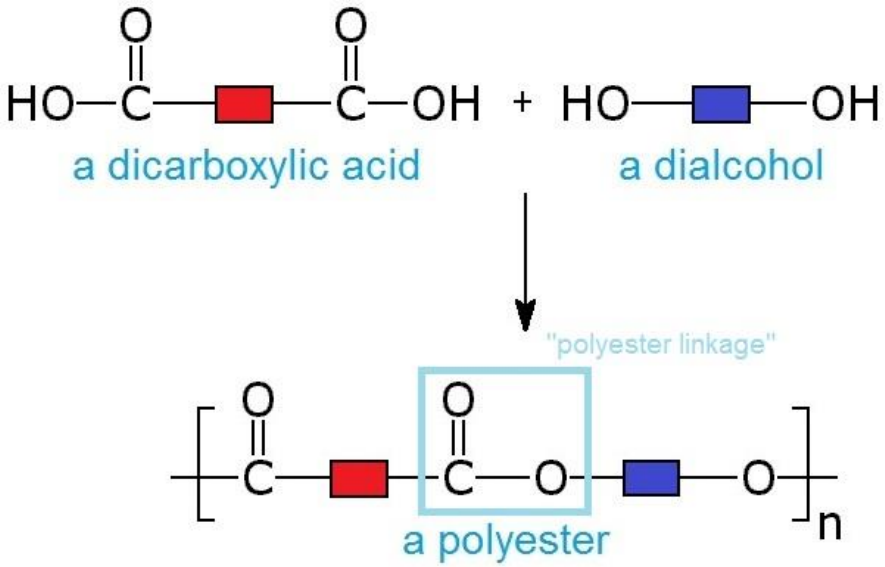


***Figure 5.13.*** *Formation of polyester with dicarboxyl acid and dialcohol (modified) [44]*

Polyester binders manufactured with diacids and diols cannot be used as a protective coating without proper crosslinking. Crosslinking of polyester chains is done with melamine derivatives most commonly with hexamethoxy methyl melamine (HMMM), shown in Figure 5.14.

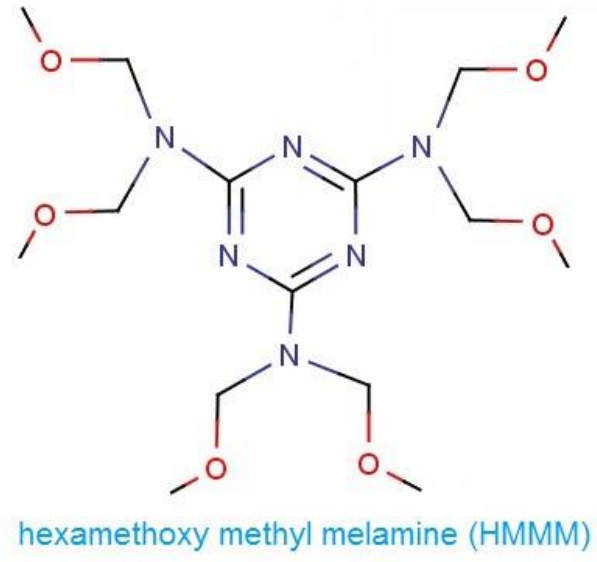


***Figure 5.14.*** *The most common crosslinker for polyester (Hexamethoxy methyl melamine, HMMM) (modified) [3]*

Compromises between different properties are necessary in order to manufacture the desired polyester binder. The amount of crosslinker in the in the system is approximately 10-35 w-% of the binder. With higher levels of crosslinker the coating becomes harder and more resistant to chemicals, but simultaneously loses its flexibility. Final properties of polyester binders are determined by the choice of the ingredients, the degree of crosslinking and the molecular weight. [3][4]

Polyester coatings can be used as a primer, a top coat or as a backing coat. Due to the lower price range of the binder it is a preferable choice for possible multilayer coatings with the TOC as a base. The reasons why polyester binders were selected for the experimental part of this thesis are that they are most commonly used binders, affordable and easily modified. With three different polyols (polyol A, polyol B and polyol C) and two different crosslinkers (melamine and isocyanate) a suitable variety of different polyester based binder systems for the study was manufactured. [4]

### 5.3.2 Polyurethane

Polyurethane coatings are more expensive than polyester coatings, but also possess much better properties. High durability and formability with excellent corrosion and UV-radiation resistance makes polyurethane coatings a widely used option for coil coat-

ing products. Polyols such as polyacrylics, polyethers or polyesters can be used with isocyanate crosslinker to achieve polyurethane linkage within the binder. Isocyanate reacts with the hydroxyl group by the way of polyaddition. The above mentioned reaction forms a structure called urethane bond, which is the recurring part of the finished polyurethane structure. The reaction between diisocyanate and dialcohol is illustrated in Figure 5.15.

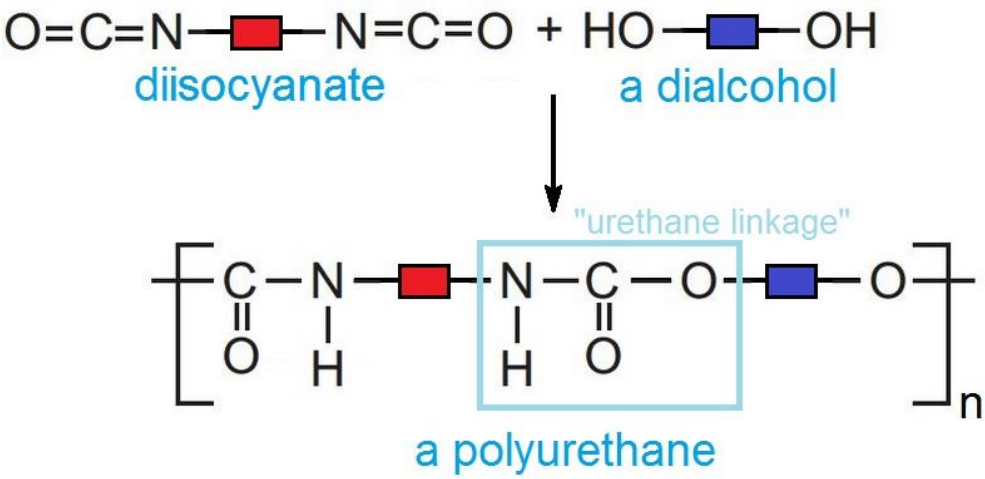


***Figure 5.15.*** *Formation of polyurethane with diisocyanate and dialcohol (modified) [45]*

Polyisocyanates, either aliphatic or aromatic, are used instead of isocyanates because of the higher functionality as crosslinkers. Polyisocyanates are also less toxic due to their larger molecular structure. In Figure 5.16 the most used isocyanates are illustrated.

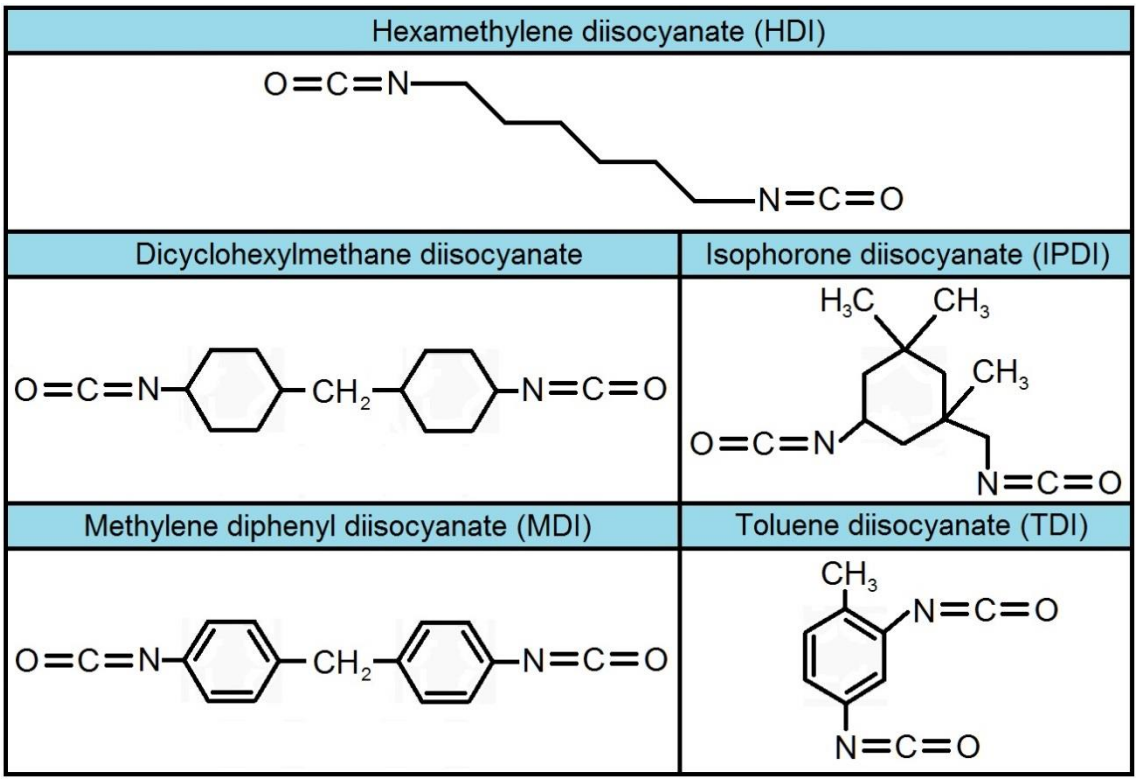


***Figure 5.16.*** *Most used isocyanates in polyurethane coil coatings (modified) [3]*

Isocyanates are a fairly reactive substance and therefore the isocyanate used for cross-linking of the binder structure has to be blocked. Blocking of the isocyanate prevents the reaction between the isocyanate and the binder prematurely. Compounds such as methyl ethyl ketoxime, ε-caprolactam or dimethyl pyrazole are used as blockers. The blocking agent evaporates in the oven at the temperatures ranging from 110 °C up to approximately 180 °C depending on the blocker used. When the blocking agent is evaporated, the reactions illustrated in Figure 5.15 starts rather quickly. Isocyanates are sensitive to moisture and form carbon dioxide if allowed to react with each other. If carbon dioxide is formed within the coating structure, pinholes can occur when the $CO_2$ leaves the system. Pinholes weaken the structure significantly and form a suitable environment for corrosion to start. [3][4][45]

The molecular structure of the polyurethane makes it possible for hydrogen bonds to be formed between the molecule chains. Due to the hydrogen bonds, the structure can absorb a significant amount of forces without the covalent bonds to break. The energy of a hydrogen bond is in the range of 20-25 kJ $mol^{-1}$, each of these bonds can be broken by outside forces without permanent damage to the coating system. Hydrogen bonds can form in different places of the structure after the force is removed, again making it possible for the system to withstand future forces. The above mentioned behavior makes polyurethane coatings quite flexible and suitable for demanding applications with high level of forming. [3][4][45]

### 5.3.3 PVdF

PVdF coatings are usually a blend of polyvinylidene fluoride and a softener called polymethyl methacrylate (PMMA). PVdF coatings are high-end products with excellent properties of corrosion resistance, UV-radiation resistance and chemical resistance as mentioned in the subchapter 2.2.1 Coil coated product at SSAB. The excellent properties are a result of the chemical structure of the coating. Compared to polyesters and polyurethanes, which are chemically cured, PVdF is physically cured and do not require a specific crosslinker in order to achieve its final structure. Although PVdF itself has excellent properties, its chemical inertness presents a challenge with adhesion and with the dispersion of pigments. High costs, low abrasion resistance and fairly high melt viscosity forces the use of a secondary polymer. As mentioned above PVdF and PMMA blends are used to optimize the properties for the application and for the final product. PMMA is highly compatible with PVdF and introduces the coating with additional properties such as good heat resistance and improved mechanical properties. The chemical structure of PVdF and PMMA is shown in Figure 5.17. [4][46]

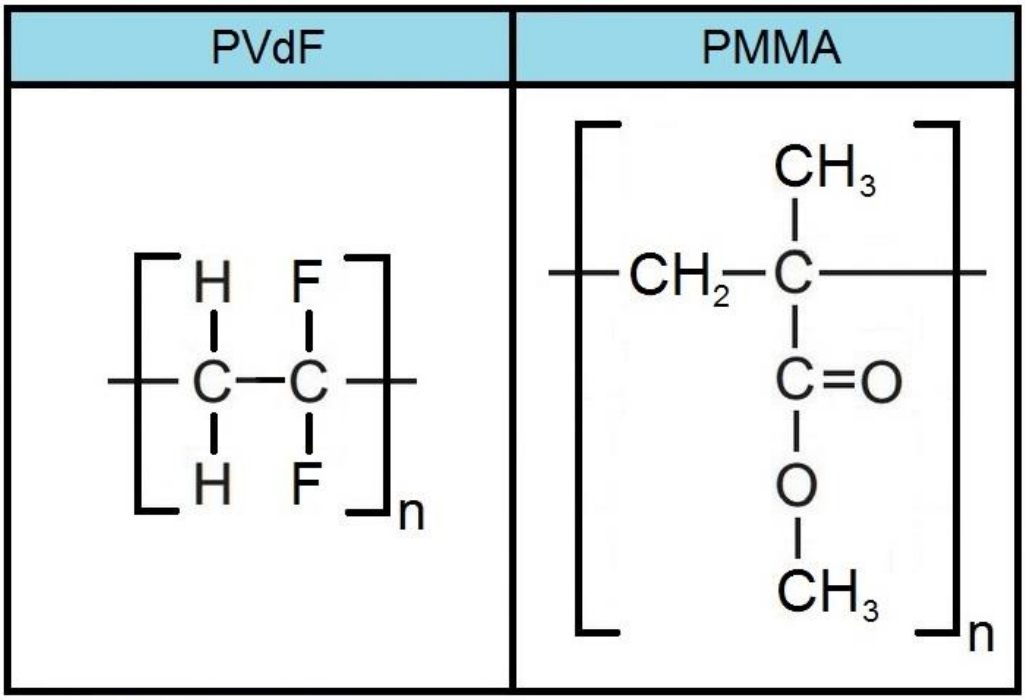


***Figure 5.17.*** *Chemical structure of PVdF and PMMA [3]*

Usually isophorone is used as a solvent and PVdF and PMMA are physically blended together. Due to the inability to include pigments in the PVdF the color pigments are dispersed in the acrylic resin (PMMA). Solvents evaporate and PVdF melts in around 230 °C. With a high temperature the PVdF is miscible with the PMMA and different ratios of PVdF and PMMA can be mixed. In most cases 70-80 w-% of PVdF is used with 20-30 w-% of the desired acrylic resin. PMT of the PVdF coating is around 249 °C, which allows the PMMA and the PVdF to form an alloy with the specific properties

mentioned above. Below the melting temperature the PVdF crystallizes and a semi-crystalline structure is formed. A study of the surface and interface properties of the PVdF and PMMA blends show that the concentration and crystallization of the PVdF is higher in the air-coating surface interface than in the bulk material. The above mentioned phenomena with the chemical structure (C-F bonds) of the PVdF are likely the causes for the excellent toughness and chemical resistance properties of the coating. [3][4][46]

The bond energies between the carbon and the fluorine atoms are significant (~485 kJ $mol^{-1}$). The harmful energy of UV-radiation (~430 kJ $mol^{-1}$) falls short of that of the bond energies, which makes the PVdF basically inert to the UV-radiation. The acrylic resin must be protected from the UV-radiation, due to the fact that PVdF does not react with the radiation and basically just lets the radiation go through to other parts of the coating system. [3][4]

### 5.3.4 Epoxy

Epoxy based coatings are quite widely used in coil coating products due to their reasonable price with excellent barrier and compatibility properties. Epoxies are a versatile binder group which can be modified easily to match the wanted requirements. Base coats and backing coats are the most common applications where epoxy binders are used. Excellent adhesion properties with metallic substrates and other binder systems make epoxy coatings a well suited choice in base coat applications. Very good mechanical properties, performance against humidity, corrosion and different chemicals govern the choice of epoxy as a primary binder system for backing coat applications. The performance of epoxy based coatings against UV-radiation limits its use as a top coat, especially in outdoor applications. Strong chalking, discoloration and loss of gloss due to light-induced degradation from the UV-radiation are the biggest downsides of epoxies. Slightly inferior properties in flexibility and in impact resistance to some of the more expensive coatings are also something to consider when choosing epoxy based coatings. [3][4][47]

Epoxy based coatings are basically diepoxies crosslinked with diamines. The diepoxy is formed from Bisphenol A (BPA) and Epichlorohydrin (ECH) with a step-growth polymerization as seen in Figure 5.18. The reaction between Bisphenol A and Epichlorohydrin can result in a pre-polymer with a high or a low molecular weight depending on the ratio of the two ingredients. With a higher amount of Epicholorohydrin in relation to the amount of Bisphenol A the polymerization degree (DP) increases. Typical DP for the epoxy pre-polymer is in the range of 12 but can vary from 1 to 25. [48]

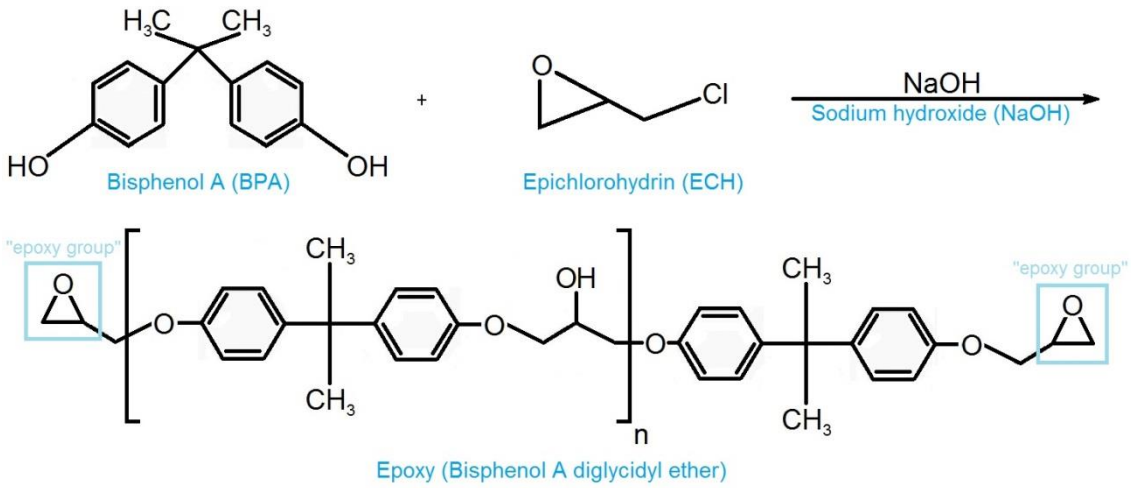


***Figure 5.18.*** *Generation of epoxy based binder (modified) [48]*

The epoxy pre-polymer needs to be crosslinked to obtain the properties that the epoxy coating is known for. Epoxies are mostly crosslinked with amines, amides, carboxylic acids and anhydrides. Most used crosslinker is a diamine that can react with the epoxy groups of the pre-polymer forming a big molecule; a crosslinked network. With different crosslinkers the density of the crosslinking can be modified and therefore the properties of the coating can be modified. Although mainly used on its own, epoxy can be mixed for example with acryl, polyester or polyurethane binders for improved properties. [3][4][48]

Epoxy coatings are not studied in the experimental part of this thesis. Epoxy as a binder is presented in the theory section of the thesis mainly because it will in future be a part of the TOC based coating system and has been a predominant choice as the backing coat for a long time. Epoxy coating will most probably be used as a base coat and as a backing coat on top of the TOC treated substrate.

## 5.4 Pigments

Pigments are one of the main components in the paint system; they do not however react with the other ingredients in the paint system. Pigments, usually fine-grained particles, are used to either give a distinctive color for the coating or add a distinctive function (usually corrosion resistance) to the coating. The pigments that give color for the coating are used for appearance and simultaneously for UV-radiation protection. Functional pigments add corrosion resistance properties, fire resistance properties or other such functionalities to the coating. Fillers are colorless pigments that are used to replace more expensive pigments and to add strength and durability to the coating. Pigments are also used to control the rheology of the paint system; the addition of pigments increases the viscosity of the system. [49][50]

Pigments used in coil coating paints are either organic or inorganic by nature. Inorganic pigments are most commonly used due to the better properties and cheaper price. Inorganic pigments are metal oxides, sulfides or metal salts. In Figure 5.19 commonly used coloration pigments are shown. Filler pigments include among others barium sulfide, calcium carbonate, silicon oxides, silicate minerals and talc. Functional pigments are usually borates, phosphates or molybdates. [49][50]


***Figure 5.19.*** *Commonly used coloring pigments (modified) [51]*

The amount and combination of pigments used for specific paint system is closely related to the wanted properties and the intended service conditions of the coating. In order to get the best possible benefits from the pigments the particles must be completely and uniformly dispersed in to the paint system. The right amount of pigments i.e. CPVC (Critical pigment volume concentration) is of great importance for the properties and performance of the coating. In Figure 5.20 the CPVC is illustrated.

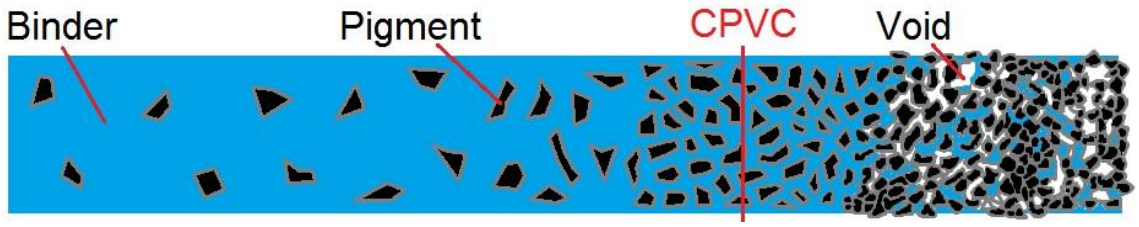


***Figure 5.20.*** *Illustration of the critical pigment volume concentration*

With a low level concentration of pigments the wanted effect of the pigments will not occur or will be significantly reduced. Pigment concentration over the CPVC level will result in voids and therefore loss of mechanical properties and increase in the permeability of the coating. Critical pigment volume concentration represents the maximum amount of pigments that can be added to the paint system so that the binder can still surround every void and empty space in between the pigment particles. [49][50]

## 5.5 Dry film formation

In this subchapter the formation of the dry film is discussed briefly. In order to understand the different variables chosen for the experimental part of the thesis, a basic understanding of the curing process is vital. The main variables in this thesis, besides the binders, are the curing process and the film thickness.

In this thesis only one layer of coating was applied on top of the TOC layer. Normally the coil coating product has at least two separate layers of coating after the pretreatment process, which means at least two separate curing cycles. In order to study the effects that the additional oven treatment has on the first layer of coating, a single and a double curing of the coating was used in the experimental part of the thesis. Curing process divides in to two separate subcategories. Both of the subcategories are represented in the curing processes of the binders used in this thesis.

Three different film thicknesses were selected for the experimental part of this thesis. In this subchapter the importance of the thickness of the coating is discussed briefly.

### 5.5.1 Curing mechanisms

Curing is the name of the process in which the applied liquid paint is converted in to a dry film with the final properties of the coating. Two separate mechanisms of curing can be observed from the binders used in this thesis. **Physical drying** (solvent loss curing) and **chemical curing** both form a similar looking dry film, but the mechanisms behind the phenomena are quite different. In coil coating process a substantial amount of energy is required to ensure the uniform curing and consistent quality of the coating. [4][52]

In the physical drying process polymer binder molecules that are disentangled in the solvent start to close-up and coalesce during the evaporation of the solvent. When the concentration of the solids grows and the concentration of the liquids drops the formation of a closed film starts. The chains of polymer that are in the remaining solution begin to mechanically entwine and form a continuous solid structure. Hydrogen bonding occurs between the molecules to further the alignment of the chains. After a specific time in elevated temperatures of the convection oven all of the solvents in the paint system have evaporated and a finished dry film has formed as illustrated in Figure 5.21. Thermoplastic coatings are physically drying, therefore giving inferior chemical and mechanical properties compared to chemically cured coatings. [4][52]

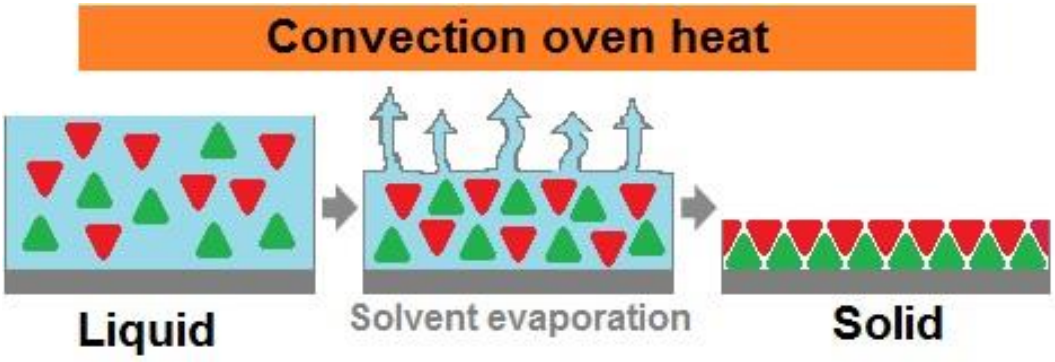


***Figure 5.21.*** *Illustration of the solvent evaporation during the curing process*

Chemical curing enables the formation of an infinite three dimensional molecular network, which consequently enables higher mechanical and chemical resistances for the coating. Chemical curing is characterized as reactions between suitable end- or side-chain groups of the polymer in order to achieve additional crosslinks between the polymer chains. The polymer obtained from the pre-reaction is usually quite small in size, but after the crosslinking of the polymer the molecular mass increases by orders of magnitude. The crosslinking and enlargement of the polymers happens via addition or condensation mechanisms. Thermosetting coatings are usually chemical cured, which explains the excellent mechanical and chemical properties associated with thermosetting polymers. [4][52]

### 5.5.2 Film thickness

In the experimental part of this thesis a set of different dry film thicknesses were tested. In a really simplified manner it could be considered that the thicker the coating the better the properties. With a higher thickness of the coating, mechanical properties usually excel, compared to thinner coatings. Although slightly improved properties, thicker coatings are much more expensive than similar coatings with lower thickness. The price of the coating in the economically challenged times, especially from industrial perspec-

tive, is one of the most significant property of the coating. With increasingly thinner coatings an adequate level of the properties could be achieved for specific purposes.

In this thesis three different film thicknesses are represented in all of the binder systems as one of the variables studied. The aim is to study the differences in the properties between varying thicknesses. Ultimately the tests should reveal the optimal dry film thickness of the selected binder and TOC combination.

### 5.5.3 Acid catalysis of polyester + HMMM system

The curing of the HMMM and polyester binder combination is a complex and dynamic entirety and is not discussed in full detail in this thesis. Nevertheless the basic understanding of the acid catalyzed reactions of the HMMM and polyester is essential in understanding the possible outcomes of the TOC + paint systems studied in this thesis. Acid catalyzed reactions are discussed mainly because of the basicity of the TOC 2 product and the fact that HMMM and polyester system requires a pH sensitive acid catalysis in order to crosslink and cure properly.

Crosslinking of the polyester based system can only occur with specific acid catalysis. The reaction rate of crosslinking of HMMM and polyester binder would be too insufficient for proper industrial applications without the use of acid catalyst. The crosslinking occurs via condensation of the HMMM with the polyester chains as illustrated in Figure 5.22. The acid catalyzed reaction is called transesterification. [4][53][54]

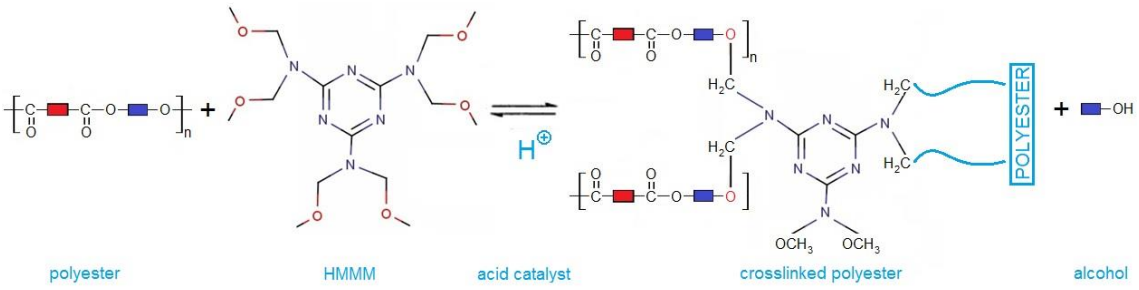


***Figure 5.22.*** *Typical crosslink of polyester chains and HMMM. The remaining metoxy groups of the HMMM can crosslink with other polyester chains ultimately forming and 3D network of crosslinked polyester*

Polyester and HMMM combination typically requires a strong acid as a catalyst. Most widely used acids are sulfonic acids of toluene and naphthalene (i.e. *p*-TSA, DNNDSA or DNNSA). The acid behaves as a catalyst and therefore remains in the final product. The reaction product, methanol, optimally leaves the product via evaporation during the curing cycle in the oven. The acid catalyst can be blocked and activated once under elevated temperatures of 120 to 140 °C. [4][53][54]

The curing times of polyester with acid catalysis could theoretically be in the range of a few seconds, but typically coil coating lines operate with a cycle of 20-30 seconds in order to properly evaporate the reaction product and solvents off the coating. The acid catalyzed reactions are highly pH sensitive and the reaction rate of the crosslinking therefore is related to the overall pH of the system. The acid makes it possible for the bonding reactions (i.e. crosslinking) between the metoxy groups of the HMMM and the hydroxyl groups of the polyester to start and accelerate to a sufficient rate. [4][53][54]

The pH sensitivity of the crosslinking process can lead to various problems, if not controlled properly. The acid catalyzed crosslinkage can hydrolyze under acidic conditions if excess humidity is present (i.e. acid rain). This hydrolysis leads to loss of network (crosslinking) structure and damage to the film. The basicity of the melamine also contributes to the absorption of acid into the film further enabling the hydrolysis to happen. The main reason for the observation of the possible hydrolysis of the crosslinking due to humidity was done because of the potential under cure (i.e. trapped water in the waterborne coating) of the TOC 2 coating. [54]

# 6. EXPERIMENTAL PART

The suitability of different binder systems on the surface of the thin organic coatings were tested in the experimental part of the thesis. The main focus was on the adhesion properties of the different binder systems with the underlying TOC. The test series were divided into two separate binder categories; polyesters and PVdFs. In the polyester category one binder system was crosslinked with isocyanate in order to manufacture a polyurethane system. The different binder systems were applied on the surface of two separate TOCs obtained from the line trials (Chapter 6.1). In the test series a number of different variables were altered to obtain a conclusive sample for the tests. In Table 6.1 selected variables and combinations are shown. In total 48 different variations were painted for both thin organic coating substrates.

***Table 6.1.*** *Variables that were used for the samples in this thesis*

| | | | |
|---|---|---|---|
| **Thin organic coating** | | | |
| TOC 1 | | | |
| TOC 2 | | | |
| **Binder system** | | | |
| **Polyester based binder** | Polyol A | + | Melamine |
| | Polyol A | + | Isocyanate |
| | Polyol B | + | Melamine |
| | Polyol C | + | Melamine |
| **PVdF based binder** | 60 %PVdF | + | 40 % Thermoplastic PMMA |
| | 60 %PVdF | + | 40 % Thermosetting PMMA |
| | 70 %PVdF | + | 30 % Thermoplastic PMMA |
| | 70 %PVdF | + | 30 % Thermosetting PMMA |
| **Dry film thickness** | | | |
| 5 µm | | | |
| 10 µm | | | |
| 15 µm | | | |
| **Curing** | | | |
| Single | | | |
| Double | | | |

Every sample was labeled with a unique code to identify the combination used for the specific sample. In Figure 6.1 the code is explained.

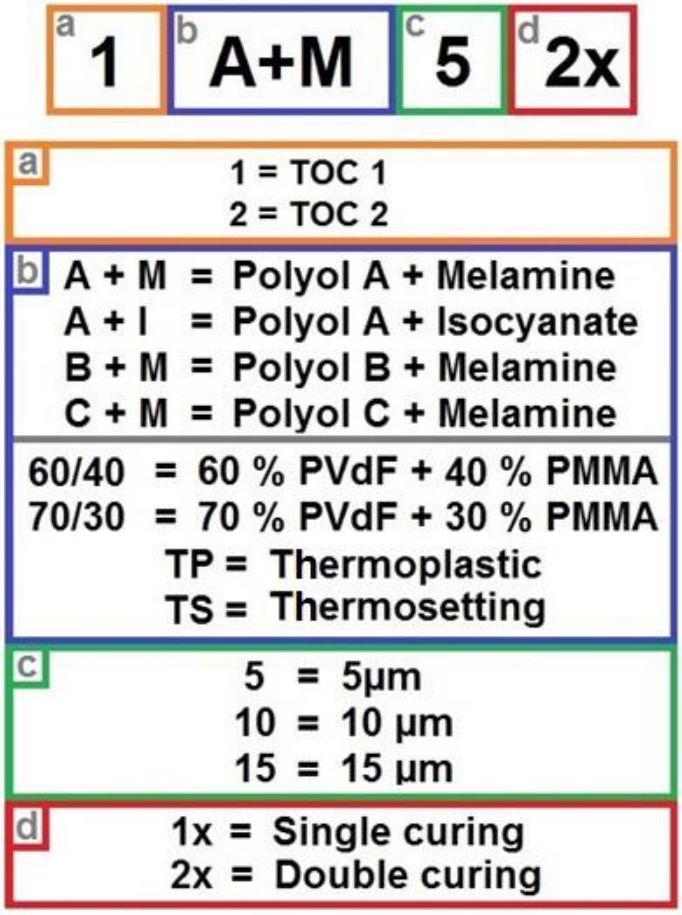


***Figure 6.1.*** *Labelling of the samples*

All of the combinations were tested using standard coating test methods explained in the subchapter 6.4 Testing methods. With the results an ANOVA-analysis was made with Matlab. The analysis was used to help with the final decisions concerning the selection of the properties for the final product. Based on the test results and the data analyzed with ANOVA-method a binder system that performed best was selected for further testing. The selection of the best coating system was made from both binder groups (polyester and PVdF) for both TOC substrates.

All of the binders were manufactured and formulated by Valspar Finland Oy. Laboratory painting and curing was done in the facilities of Valspar. Tests for the coatings were administered in Hämeenlinna at the research and development laboratory with the guidance of the laboratory staff. All of the paints used in the first test sets were simplified to include just the essential ingredients. As much as possible of the additives were removed to control the amount of variables. For the final test set with the best possible coating systems the paints were manufactured with all of the ingredients commonly

used in real commercial products. In this chapter the line trials, painting process and testing methods are discussed.

## 6.1 TOC steel strip and the success of TOC coating process during the line trial

Line trials for both of the selected thin organic coatings were prepared and planned by SSAB Europe. First line trial was run at 4.12.2014 and the second one at 18.12.2014. In both of the line trials a representative from the manufacturer of the TOC in question was present. The line trials were a part of an ongoing research of thin organic coatings for the HYBRIDS project. In the research project two separate coating systems (Hiarc and Purex) were painted on top of the thin organic coatings.

### 6.1.1 TOC 1 line trial

TOC 1 was applied with the pretreatment equipment (spray and squeeze). The optimal amount of the pretreatment liquid was researched in earlier laboratory trials with the representative of the manufacturer. With the results from the earlier tests and with expertise of the manufacturer, the target weight range for the pretreatment primer layer was set at 9-22 mg P /$m^2$. For economic reasons the aim was to apply approximately 10 mg P / $m^2$.

With the manufacturer's instructions the dilution of the TOC chemical was prepared for the first trial with 40% concentration. After the first part of the coil, a sample was taken and a portable X-ray fluorescence (XRF) spectrometer was used to analyze the sample. Slightly too low results were obtained and a dilution of 60 % was mixed for the second part of the coil. With the 60 % dilution the results with the XRF were promising, although quite significant variations were observed. According to the measures a dry film of 1.4 g / $m^2$ (~10 mg P / $m^2$) was achieved. Concentration of 60 % was used for the rest of the trial. The results from the standard line tests done to the Purex and Hiarc coatings showed promising results. [55]

Because of the above mentioned variations from the portable XRF measures, a series of tests was made in Top Analytica after the line trial of the TOC 1 in order to further study the dispersion and structure of the coating layer. XRF measures of Ti, Si and P were administered for the TOC 1 samples. Secondary ion mass spectrometry (SIMS) was used to determine the composition of the TOC 1. In order to establish if the distribution of the coating was successful, other measurements with different equipment such as electron probe microanalyzer (EPMA) and energy-dispersive X-ray spectroscopy (EDS) were administered. Both 40 % dilution samples and 60 % dilution samples were tested, but the emphasis was on the optimal 60 % samples. [56]

TOC 1 showed a surprising pattern when the SEM images were analyzed. As seen in Figure 6.2 the somewhat regular pattern on the TOC 1 had enriched spots of Si and P, which were measured with the EDS. The spots were not visible with stereo microscope, but very distinctive in the SEM images. [56]

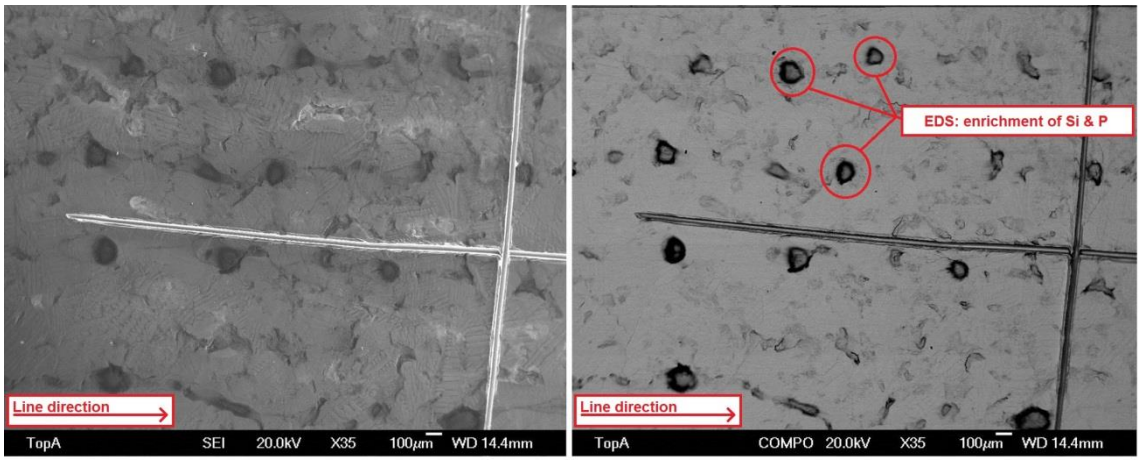


***Figure 6.2.*** *SEM images from the top side of the TOC 1 coating. Patterns show enrichment of Si and P in the surface (modified) [56]*

SIMS measurements from the area of the spots were also administered. SIMS measurements showed similar enrichment of Si in the spots. Outside the spots Ti, Ca, F and P were detected as seen in Figure 6.3.

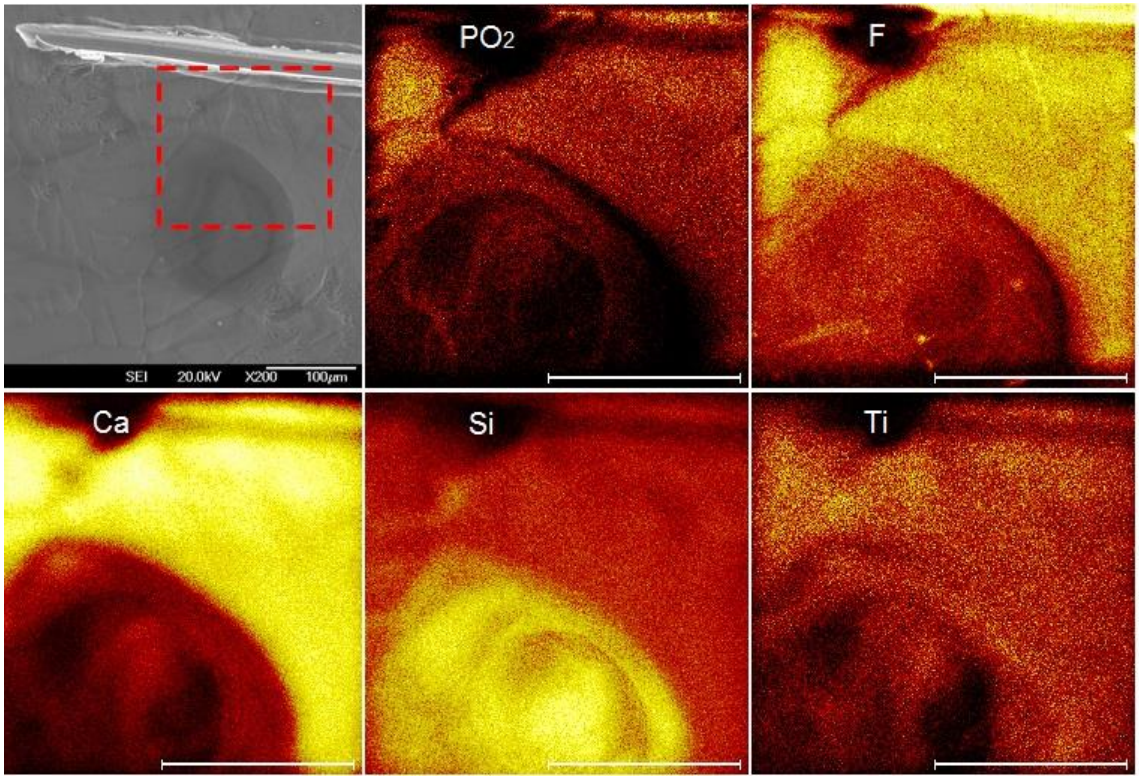


***Figure 6.3.*** *SIMS measurements from the top side of the TOC 1 coating. Spot shows enrichment of Si. The area outside of the spot shows other elements such as Ca, F, Ti and P (modified) [56]*

From the earlier laboratory scale studies with similar TOC product (trivalent chromium product from the same manufacturer) the above seen pattern i.e. segregation was not detected. The distributions of different trace elements (Ti, Si, P) in the TOC 1 were measured with EPMA and XRF. With the XRF measurements the width of the sample panel was divided into six separate regions. From the edge regions (left and right edge of the coil) six separate measurements were taken as well as three from the middle regions. With EPMA approximately 2000 point were measured across the width of the sample panel. Both methods show significant variations of the concentrations of the trace elements throughout the surface area of the TOC 1 product. [56]

Average distribution of phosphorous from the measurements above was calculated to be 11.2 mg / $m^2$, which is in the ideal range set by the manufacturer. Although the average value of the distribution of phosphorous is in the ideal range, the variation was relatively high being between 7-16 mg P / $m^2$. The samples for this thesis were taken from the last coil that was run in the line trial. Same part of the coil than was used for the experimental part of this thesis was measured with the above mentioned tests. [56]

### 6.1.2 TOC 2 line trial

TOC 2 was applied with the primer coater (two-roll coater). The optimal wet film thickness was researched in earlier laboratory trials with the representative of the manufacturer. With the results from the earlier tests and with expertize of the manufacturer, the target weight range for the TOC layer was set at 2,5 g/m$^2$, which corresponds to a gauge of 1,5 µm.

The optimal thickness for the TOC 2 was achieved in the line trial. The gauge of the coating was measured with a XRF analyzer; calibration samples from the manufacturer were used. Line-laboratory results showed promising results in mechanical and visual testing. MEK and Stripper test results however were significantly below the accepted limit in Purex system, which usually points at an unsuccessful curing of the coating. The PMT of the Purex system was raised during the line trial in order to properly cure the coating on top of the TOC 2 substrate, nonetheless the MEK and Stripper test results remained on unsatisfactory level. PVdF based Hiarc coating showed really good results from all of the line-laboratory tests.

The poor MEK and Stripper test results were observed during the line trial and studied in numerous ways after the line trial ended. Further testing on the subject was conducted in Top Analytica. A slightly too low PMT for the TOC was considered to be the most probable reason for the poor MEK and Stripper test results.

The XRF measures showed an even distribution of titanium throughout the width of the coil with 223-242 mg/m$^2$ average values. Titanium particles were evenly distributed inside the coating as seen in the SEM image of the TOC 2 in Figure 6.4.

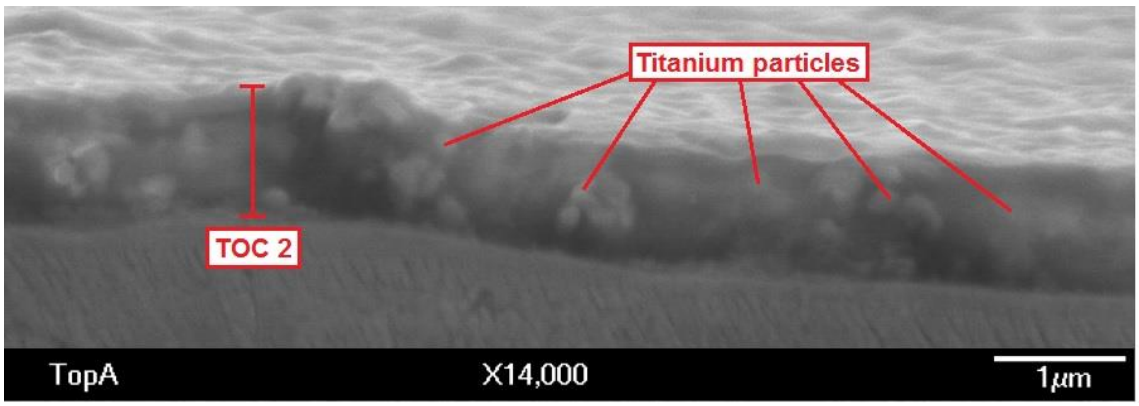


***Figure 6.4.*** *SEM-image of TOC 2 coating with evenly distributed Ti-particles (modified) [57]*

The samples for this thesis were taken from the first coil in the line trials and the results for the samples are comparable to the values mentioned above. [57]

## 6.2 Laboratory painting and curing process of the first set

Samples for the experimental part were cut to dimensions of 20 x 30 cm. Test samples of the coatings were painted in order to establish the optimal PMT (peak metal temperature) and curing time in the oven. The simplified paints were applied on traditionally pretreated steel sheets as a baseline for the curing times and the choice of applicator rods. With the preliminary tests, a set of information was gathered. Some minor changes were made to successfully paint the samples for the experimental part of the thesis.

Painting process was done with specific applicator rods for each film thickness. The basic principle of the applicator rod is shown in Figure 6.5. The grooves between the coils of wire spread the right amount of paint on the surface of the substrate.

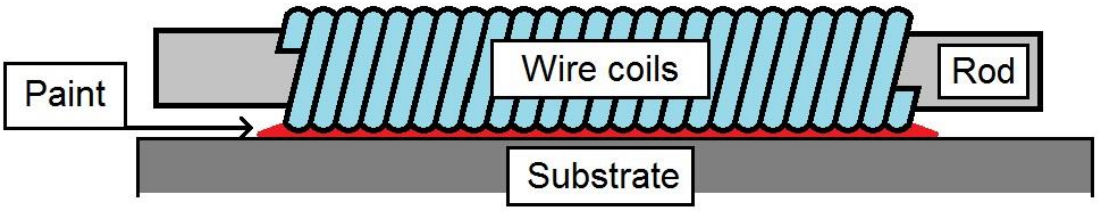


***Figure 6.5.*** *Illustration of an applicator rod*

The sample sheet was first cleaned from impurities with a cloth and then placed on a magnetic table for the painting process. Approximately a width of 1.5 centimeters of paint was administered on the upper part of the sample sheet. The applicator rod was properly wet on top of the applied paint layer with a few back and forth motions. A gentle force and a constant velocity were used to pull the applicator rod through the sample sheet. Immediately after the painting process the samples were taken to the oven (Fresenberger CC625) for curing. Specific oven cycles were used for each of the different samples to achieve optimal curing. After the oven cycle the samples were quenched in water and air dried. In Figure 6.6 the newly automated oven used in this thesis is shown.

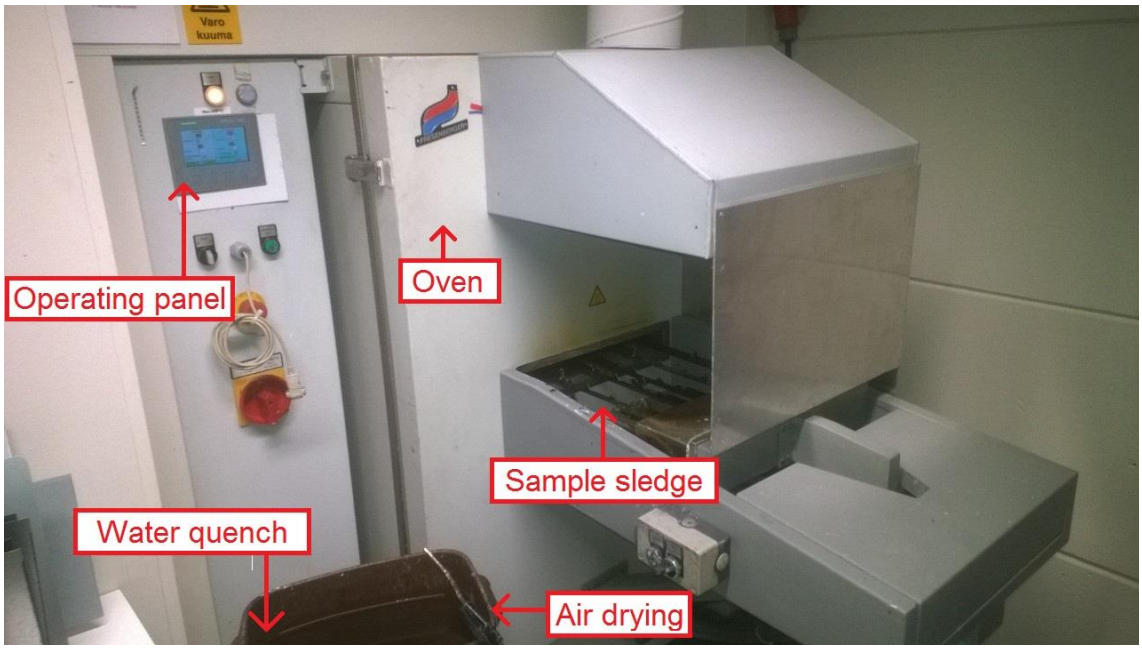


***Figure 6.6.*** *Fresenberger CC625 oven*

Each of the finished samples was measured with Fischerscope MMS 3 AM to check for the uniformity of the film and the overall thicknesses of the coating. The desired thicknesses of 5 µm, 10 µm and 15µm were met with an accuracy of approximately ±2 µm.

### 6.2.1 Polyester based coating systems

Polyesters with melamine as a crosslinker were cured with a PMT of approximately 232 °C with an oven cycle of 36 seconds. Reatec PMT-strip as illustrated in Figure 6.7 was used to measure the PMT from the sample. A random testing with the PMT-strip was done during the painting process to ensure a uniform quality.

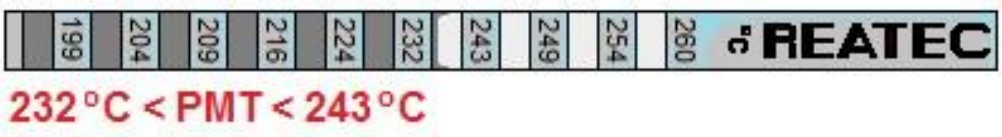


***Figure 6.7.*** *REATEC PMT-strip illustrating a PMT measuring range from 199 °C to 260 °C*

In the case of isocyanate as the crosslinker a cycle of 40 seconds was used in order to achieve a PMT of approximately 250 °C. The coil coating oven was recently automated and the lengths of the curing cycles were programmed directly to the machine. The temperature of the oven was 320 ± 3 °C and the fan was operating at a speed of 2000 rpm for each of the polyester coatings. Averages of the coating thicknesses were 6.0 µm, 10.5 µm and 15.8 µm for polyester in both the TOC 1 and TOC 2 samples. A total of three A4 sized samples for each combination were painted. The low-thickness paint layer was applied with an applicator rod 27 or 32, the mid-thickness paint layer with 41

or 50 and the high-thickness paint layer with 60, 64 or 69. MEK and Stripper tests were administered to check if the curing process was successful.

### 6.2.2 PVdF based coating systems

PVdF coatings were cured with a PMT of approximately 254 °C with an oven cycle of 40 seconds. Temperature of the oven was 320 ± 3 °C and the fan was operating at a speed of 2000 rpm for each of the PVdF coating combinations. Averages of the coating thicknesses were 5.8 µm, 10.6 µm and 15.1 µm for PVdF in both TOC 1 and TOC 2 samples. A total of three A4 sized samples for each combination were painted. The low-thickness paint layer was applied with an applicator rod 27 or 32, the mid-thickness paint layer with 50, 55, or 64 and the high-thickness paint layer with 64, 73 or 78. MEK and Stripper tests were administered to check if the curing process was successful.

## 6.3 Second set and reference samples

The reference samples were selected and painted after the first set of the coating combinations was tested. The test results of the painted combinations revealed the best possible combinations of film thicknesses, oven cycles and binders for both TOC 1 and TOC 2 substrates. The best coating systems were selected for further testing and the reference samples were painted with these coating systems. References were painted on top of a normal pretreatment (spray and squeeze) and on top of “dry” zinc without pretreatment. The aim was to assess the importance of the pretreatment to the primer compared to the system where these layers were replaced with the TOC 1 and TOC 2 coatings. In this thesis the adhesion properties and humidity resistance were the main methods of assessing the role of the pretreatment and primer. Same tests that were performed for the first set were also done to the second set and for the reference samples.

The second set of coatings was painted with exactly the same specifications as the first set. In order to ensure a uniform quality and proper curing, a PMT-strip was used to measure the PMT obtained with the specific oven cycle.

## 6.4 Testing methods

In this thesis a number of different laboratory tests were administered for each of the coating combinations. The main focus on all of the testing methods was on the adhesion of the applied coating layer with the underlying TOC. The aim of the testing was to measure the adhesion of the different coating systems and simultaneously see how the differences in the coatings correlate to the performance in the humidity tests. The tests for this thesis were selected to be similar of those done in the earlier TOC research mentioned in the chapter 4. Thin organic coatings. In this subchapter all of the used testing methods are presented.

### 6.4.1 Film thickness

The film thickness was measured with a Fisherscope MMS 3 AM as seen in Figure 6.8. The film thickness test was done based on the standard EN 13523-1:2001.

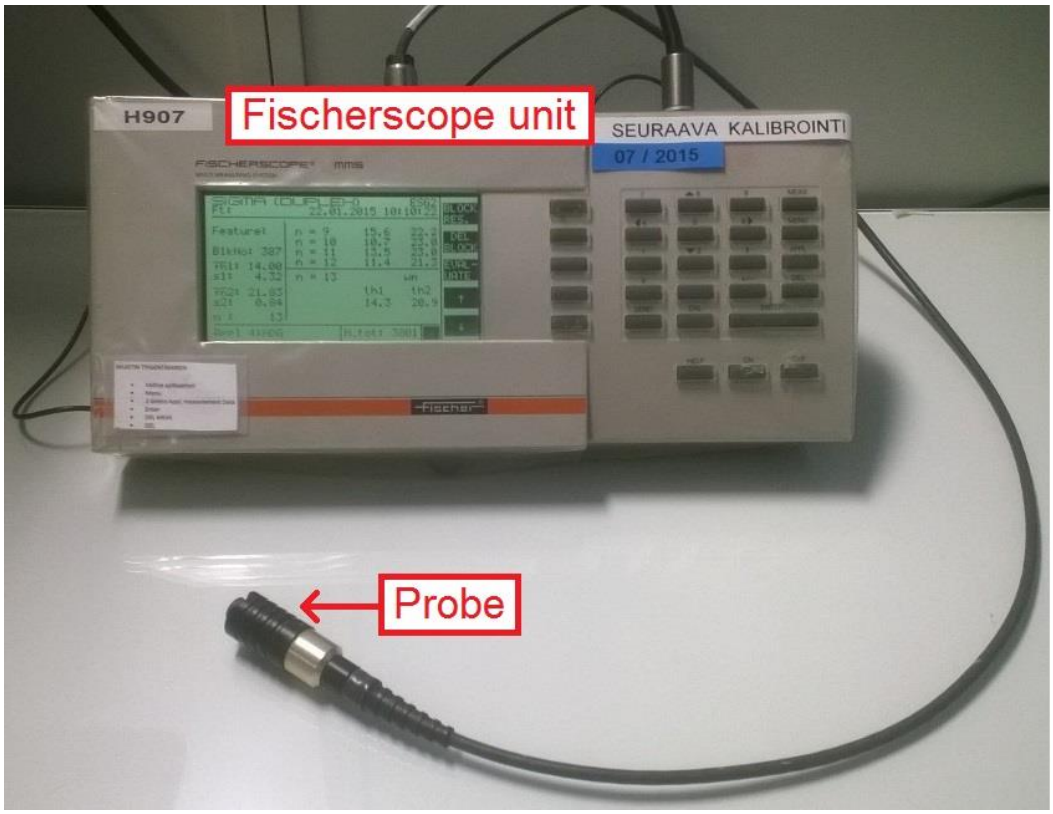


***Figure 6.8.*** *Fischerscope MMS 3 AM film thickness measurement apparatus*

Fischerscope MMS 3 AM uses magnetic induction and eddy currents to assess the thickness of both the metallic and the organic coating. The apparatus was calibrated according the specifications of the manufacturer, so that the thickness of the zinc layer was deducted from the final result. Film thicknesses were measured from 12 different points of the sample and an average of the results was calculated for each sample. The results were given in the average values from all samples of the same coating specifications (film thickness, binder, oven cycle). This test method was mainly used to determine the choice of the applicator rod and the assessment of the uniformity of the samples. In this thesis only NDT (non-destructive testing) methods were used to assess the thickness of the dry film.

### 6.4.2 Resistance to cracking on bending (T-bend)

The flexibility of the coating and the loss of adhesion when exposed to bending were measured with a T-bend test. T-bend test measures the resistance to cracking of an organic coating applied on top of a metallic substrate. The test was done based on the

standard EN 13523-7:2014. As can be seen in Figure 6.9 the conically bent sample represents bending radii from 0T upwards to nT depending on the length of the sample. [58][59]

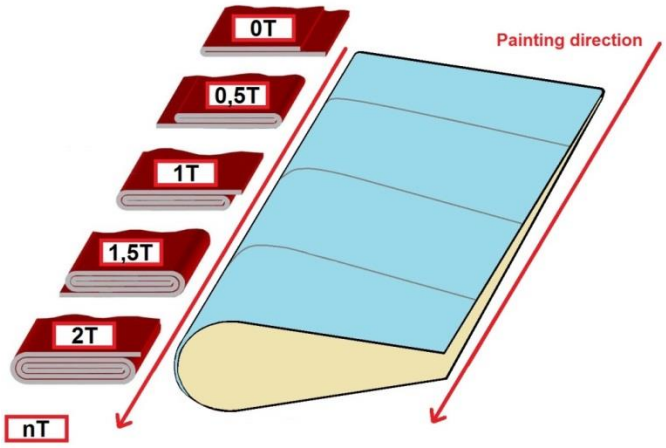


***Figure 6.9.*** *Illustration of the sample for the T-bend test. Different bending radii are represented in the conically bent sample*

In the experimental part of this thesis a sample of 10 cm x 15 cm was prepared from all of the coating combinations. As illustrated in Figure 6.9 the painting direction is perpendicular to the fold. The fold was done first with a pre-fold to approximately 90 degrees, followed by a conical fold with a specific apparatus. Illustration of the T-bend test and all of the necessary variables are shown in Figure 6.10. [58][59]

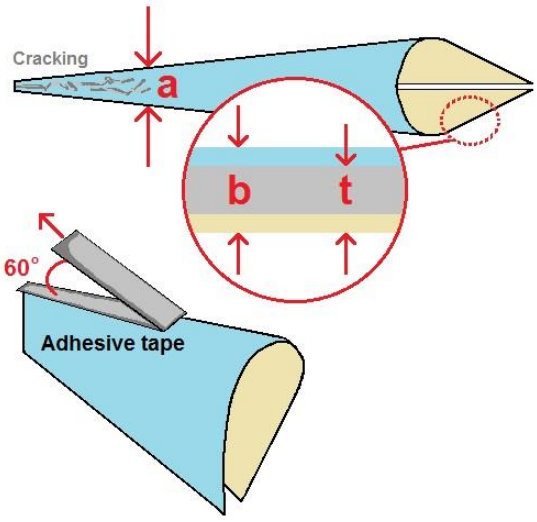


***Figure 6.10.*** *Illustration of the T-bend test and the variables needed to determine the flexibility (resistance to cracking) and adhesion of the bend sample*

The bent side of the sample was examined with a 10 x magnification. The gauge *a* [mm] of the sample from the location of the farthest crack was measured with a caliper. The

final value of the T-bend test for flexibility was calculated with the following equation 6.1.

$$T = \frac{a - 2b}{2t}, \qquad 6.1$$

where *T* [T] is the flexibility (resistance to cracking) of the coating, *b* [mm] is the thickness of the sample (substrate, metal coating, organic coating) and *t* [mm] is the thickness of the sample without the organic coating. According to the standard the results are given with an accuracy of 0.5 T, in this thesis the results were given with 0.1 T accuracy in order to get more versatile results for the ANOVA-method. [58][59]

The loss of adhesion was measured after the flexibility of the coating had been determined. A 25 mm wide transparent pressure-sensitive adhesive tape was applied along the length of the bend. The adhesive tape was rubbed firmly with a finger to ensure a good contact between the sample and the tape. The tape was removed with a steady pull of approximately 0.5 - 1 s at an angle of 60 ° to the sample. The T value was calculated with the equation 6.1. The variable *a [mm]* was measured from the point where no pealing (removed organic coating stuck to the adhesive tape) of the coating was observed. [58][59]

### 6.4.3 Resistance to rapid deformation (impact test)

Resistance to rapid deformation and the loss of adhesion after the deformation was measured with an impact test. Impact test was done based on the standard EN 13523-5:2014. Impact test was carried out with an apparatus that enables a constant and commutable force to be applied on the sample. In this thesis a hemispherical weight with a mass of 900 g and a diameter of 15.9 mm was used. The weight was dropped on the reverse side of the sample sheet from different heights in order to form a rapid deformation to the sample. Illustration of the impact and the deformation of the sample sheet can be seen in Figure 6.11. [60][61]

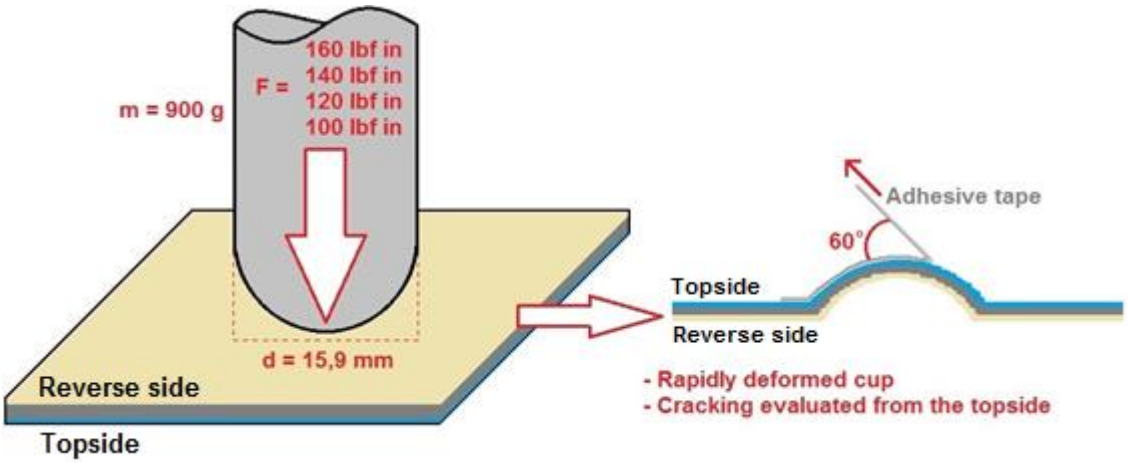


***Figure 6.11.*** *Illustration of the rapid deformation of the sample on impact a testing method for adhesion loss*

The standard test would show either a pass/fail result with a specific force or the specific force that would not result in a cracking of the organic coating. The variations of the results from the standard test would be minor and a proper comparison with ANOVA-method would be impossible. The standard testing method was modified in order to achieve more versatile results. The testing apparatus was used as is advised in the standard, but a slightly different way for the interpretation of the results was created. [60][61]

In the experimental part of this thesis the following method of interpretation of the results was used. Impacts that equal the force of 160, 140, 120 and 100 lbf in (1 J = 1 Nm = 8,8 lbf in) were administered for each of the samples. The resulting cracking from the impacts to the coatings were evaluated with a scale of 1-5 (1 = intact, 2 = singular cracking, 3 = minor cracking, 4 = average cracking, 5 = severe cracking) from the center and the borders of the deformation. For each impact an average of the two scores were calculated. Each sample was finally scored with the sum of each of the scores from the four different drops. Each of the samples was evaluated with a score ranging from 4 to 20, the lower the result the better the resistance. [60][61]

The adhesion loss measurements as described in the standard were done without any modification. The adhesion loss (pealing) when exposed to rapid deformation was measured with a 25 mm wide transparent pressure-sensitive adhesive tape. The tape was firmly rubbed against the deformed cup and pulled off steadily at an angle of 60 degrees. The result for the adhesion loss was presented as the highest force (lbf in) that the coating can withstand without pealing. [60][61]

### 6.4.4 Resistance to humidity (QCT)

Resistance to humidity and resistance to humidity when exposed to different bending radii were measured with a QCT test. The testing method used is based on the standard

EN 13523-25:2014. In QCT tests the samples are exposed to a continuous humidity in elevated temperatures. A cycle of 1000 h or 1500 h are used with the corresponding temperatures of 60 ± 5 °C and 38 ± 2 °C. The relative humidity for both cycles is approximately 100 %. In this thesis a cycle of 1000 h with a temperature of 60 ± 5 °C was used. [62][63][64]

Results from the test were assessed with the aid of a separate reference guide for blistering as seen in Figure 6.12. The blistering was assessed based on the density and size of the blisters. A score of 2, 3, 4 or 5 was given for both of the attributes. Most severe blistering based on the above mentioned scoring system is 5(S5). If the sample does not show any signs of blistering a score of 0 can be given. [62][63][64]

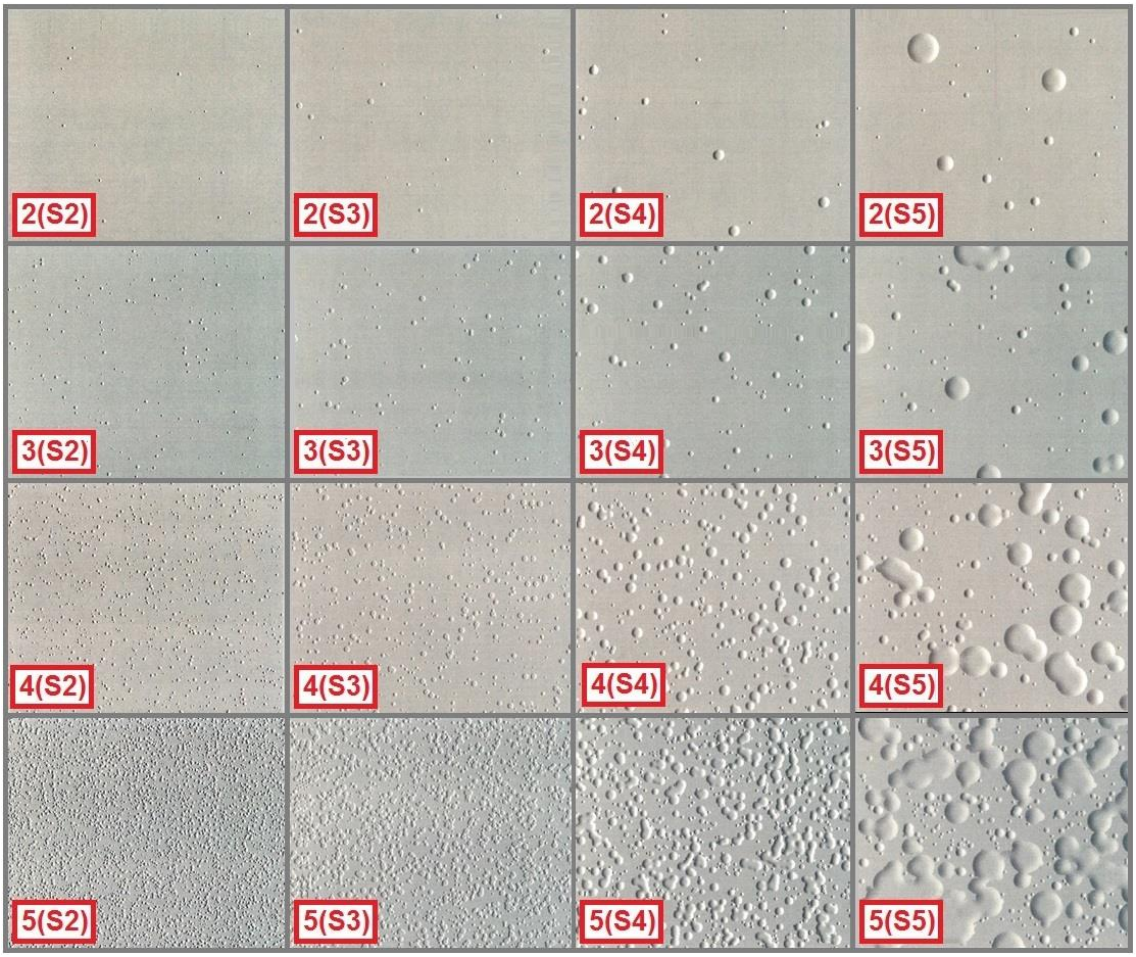


***Figure 6.12.*** *Guide for assessing the degree of blistering based on size and density (modified) [62]*

In the QCT test a checking of the samples was done in 250 h intervals. Each of the samples was evaluated according to the above mentioned method on each interval. Other irregularities and damages (rust, cracking, loss of color) done to the samples were also reported. Separate wet and dry adhesion tests were performed after the full cycle of

1000 h was finished. Wet adhesion was done immediately after the completed cycle and the dry adhesion test a week after the QCT cycle; wet and dry adhesion tests are identical with the standard impact test. Wet and dry adhesion tests were done only for the second set of samples with 160 lbf in impact. [62][63][64]

### 6.4.5 Success of the curing process (MEK & Stripper)

The resistance to solvents in rubbing was determined with a MEK test, which is a test based on the standard EN 13523-11:2011. The MEK test was used to determine if the curing process was successful. The samples were tested for proper curing because of the problems faced in the line trial of the TOC 2 coating. In the testing of the line trial coatings at the line laboratory the MEK test failed with the TOC 2 + Purex system. All different paint systems in this thesis were tested with MEK. MEK test consist of a back and forth rubbing of the coating with a cloth soaked in approximately 10 ml of methyl ethyl ketone (MEK). In the rubbing process the applied pressure should be in the range of 0.05 ± 0.01 MPa with a surface area of 100 $mm^2$ to 200 $mm^2$. The above mentioned pressure and surface area specifications correspond to approximately a mass of 0.5-1 kg with a finger wrapped in a cloth. The result of the MEK test is given in a number of double strokes the coating withstands; the maximum being 100 double strokes. In Figure 6.13 the results of a passed and failed MEK test are demonstrated.

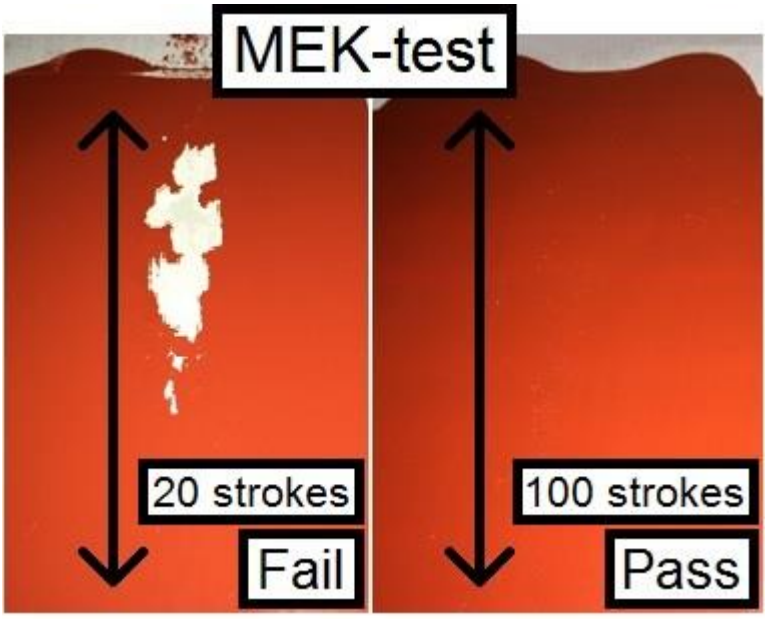


***Figure 6.13.*** *Pass and fail results of a MEK test (modified) [65]*

The strokes should be at least 7.5 cm long. When the top coat was worn off and the primer layer (in this thesis the TOC layer) shows the number of back and forth strokes used were reported. [66][67]

The successfulness of the curing process can also be assessed with a **Stripper test**. Stripper test is not directly based on any standard, but rather on years of experience on the resistance of solvents in coil coatings. Stripper 100 -paint remover was applied to a cross shaped cut, which penetrated the organic coatings and reached the zinc layer. The successfulness of the curing process was assessed based on the time the organic coating withstood the Stripper without deteriorating. In Figure 6.14 the results of a passed and failed Stripper test are demonstrated.

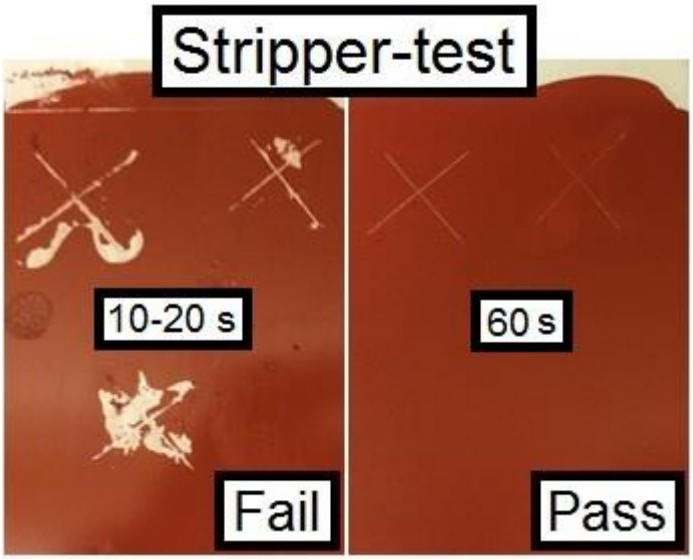


***Figure 6.14.*** *Pass and fail results of a Stripper test (modified) [65]*

The curing process is considered to be successful if the organic coating can withstand over 60 seconds without blistering. If the organic coating starts to blister in between 30 and 60 seconds, the curing process is considered to have been somewhat successful, if a time of less than 30 seconds is achieved the curing process is considered to have been a failure. [68]

## 6.5 Statistical analysis (ANOVA)

In this subchapter the statistical analysis used in this thesis is explained. An adequate amount of the theory behind the method is opened, because a basic understanding of the method used is vital for understanding the results and the conclusions drawn from the results.

ANOVA is a statistical analysis of data, which determines if three or more groups share an equal mean value. The ANOVA (Analysis of Variance) compares the amount of variation in the measured data between the separate groups, with the amount of variation within the groups. With ANOVA the data is calculated and determined if the differences among the data groups are greater than that caused by chance. If the differences are greater, the groups can be ruled to have significantly different means and therefore cate-

gorized as truly different groups. In the following Figure 6.15 the difference of the terms “between group variance” (Between-group sum of squares, BSS) and “within-group variance” (Within-group sum of squares, WSS) is illustrated. [69]

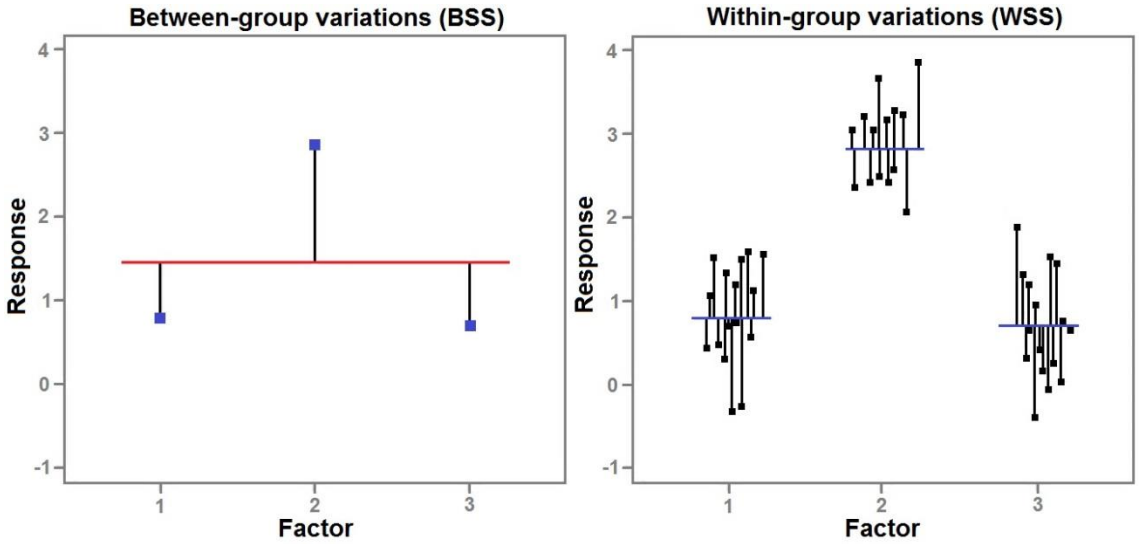


***Figure 6.15.*** *Illustration of the between-group variations and within-group variations (modified) [69]*

The figure above is an illustration of three different groups to be analyzed with ANOVA statistical analysis. The chart on the left shows the overall mean value of the data with a red line and the individual group means with blue boxes. In the chart on the right the blue lines show the group means and black boxes show the individual data values. The black lines in both charts show the deviations (i.e. variance) of the data. [69]

The above mentioned method of analyzing the results was chosen in order to statistically prove the differences in properties due to the chosen variables in this thesis. If there could be found a statistically proven difference in the population marginal means of different groups, the groups that differ can be arranged and categorized based on the values of the data. This method was used in this thesis to determine which of the binders to choose for the final product. ANOVA-method was also used to statistically compare which film thickness and curing cycle to use with both of the TOC substrates.

To understand the results given in subchapter 7.3 ANOVA the following theory is important to understand. ANOVA as a mathematical equation 6.2 is as follows:

$$x_{ij} = \mu_i + \varepsilon_{ij}\,, \qquad 6.2$$

where *x* is the individual data point, subscript *ij* denoting the group and the individual observation. ε is the unexplained variation (i.e. chance, error) and μ parameters are the population means of each group. [69]

ANOVA calculates a test statistic, the F-ratio of the data. A hypothesis is made, usually a null hypothesis, which assumes that all the groups share an equal mean. With the F-ratio a probability (p-value) can be determined and used to either reject or confirm the null hypothesis. If the null hypothesis is rejected the outcome that the hypothesis states is very unlikely to happen. In this thesis a p-value less than 0.05 is considered to reject the null hypothesis. When the p-value is less than 0.05, there is a mere 5 % probability for the statement of the null hypothesis to happen. [69]

The calculations behind the ANOVA-method consist of a few steps, which are demonstrated in the following equations 6.3. A variation between three different groups was used to demonstrate the above mentioned method. The variance (i.e. sum of square) between the groups (BSS) is calculated as follows:

$$BSS = n_1(\bar{x}_1 - \bar{x})^2 + n_2(\bar{x}_2 - \bar{x})^2 + n_3(\bar{x}_3 - \bar{x})^2, \qquad 6.3$$

where the equation consists of the square of the differences between each group mean ($\bar{x}_1, \bar{x}_2, \bar{x}_3$) and the overall population mean ($\bar{x}$), multiplied by the sample size ($n_1, n_2, n_3$). A form for the BSS that is used to calculate the F-ratio of the data is the mean between-groups sum of squares (Mean-BSS), which is calculated by dividing the BSS with the degrees of freedom (*d.f.* = n-1).

The variance within-groups (WSS) is calculated with the following equation 6.4:

$$WSS = s^2_{group\ 1}(n_{group\ 1} - 1) + s^2_{group\ 2}(n_{group\ 2} - 1) + s^2_{group\ 3}(n_{group\ 3} - 1), \qquad 6.4$$

where the equation consists of the sum of variance of each group ($s^2_{group1}$, $s^2_{group2}$, $s^2_{group3}$) times the degrees of freedom in each group ($n_{gruop1}$ *-1*, $n_{gruop2}$ *-1*, $n_{gruop3}$ *-1*). Again the needed form is similar to the one with BSS so the WSS is divided by the total degrees of freedom, resulting in a mean within-group sum of square (Mean-WSS). [69]

F-ratio is a ratio between the Mean-BSS and Mean-WSS. If the difference between the groups is similar to the difference within the group the F-ratio has a value of approximately 1. When the average difference between groups becomes greater than that of the average difference within the groups the F-ratio has a value greater than 1. The p-value (probability of the null hypothesis to be confirmed) rises when the F-ratio approaches the value 1. When the F-ratio rises the p-value approaches the value 0, and when the p-value is under 0.05 the null hypothesis is rejected and the population marginal means of the different groups are considered to be significantly different. [69]

The above mentioned calculations were done with Matlab, providing this thesis a means of analyzing the testing data. The calculations and figures were done using the testing data discussed in the subchapter 7.2 Mechanical properties. The results and conclusions of the analysis are discussed in the subchapter 7.3 ANOVA.

# 7. RESULTS

The best possible first layer coating for both of the TOC substrates was selected with extensive testing. With the first sample set of 96 different combinations, a selection of mechanical resistance and humidity resistance tests were administered. In order to narrow down the most potential combination of binder, film thickness and curing cycle an ANOVA analyze was done and the results were used as a support for the decision.

In this chapter the mechanical and humidity test results are discussed in detail and the reasons for the choices during the experimental part are explained. The results from the ANOVA analyze are also explained and discussed.

## 7.1 Compatibility between the binders and the TOCs

The curing of the Purex system on top of the TOC 2 was somewhat unsuccessful as mentioned in the previous chapters. Because of the line-laboratory´s MEK and Stripper tests for the Purex + TOC 2 system, which led to failed results, all of the binder systems in this thesis were tested for the successfulness of the curing. The failed MEK and Stripper test results were considered to originate from the curing of the TOC 2, rather than the top coat paint itself. The successfulness of the curing was nevertheless tested and similar observations were done with the binder systems used in this thesis that was done with the line trial materials.

MEK and Stripper tests were performed for all of the binder systems with 10 µm thicknesses and with a single and a double oven cycle. Stripper test results were successful and the coatings were undamaged with a full 60 second cycle of exposure. Amongst the samples only one binder system on the TOC 2 substrate, Polyol C + Melamine, failed the Stripper test with less than 5 seconds of exposure until permanent damage. With the said sample the Stripper test result was slightly better with double oven cycles, but still reaching only about 10 seconds of exposure. The MEK test results were varying from excellent results to really poor results. The results from the MEK tests are presented in the Table 7.1.

***Table 7.1.*** *Results from MEK and Stripper tests*

| Sample | THIN ORGANIC COATING | Thickness [µm] | Stripper (single oven / double oven) [s] | MEK (single oven / double oven) [rubs] |
|---|---|---|---|---|
| A+M | 1 | 10 | 60 / 60 | 100 / 100 |
| A+M | 2 | 10 | 60 / 60 | 60-65 / 75-80 |
| A+I | 1 | 10 | 60 / 60 | 100 / 100 |
| A+I | 2 | 10 | 60 / 60 | 100 /100 |
| B+M | 1 | 10 | 60 / 60 | 100 / 100 |
| B+M | 2 | 10 | 60 / 60 | 15-20 / 30-35 |
| C+M | 1 | 10 | 60 / 60 | 100 / 100 |
| C+M | 2 | 10 | 5 / 10 | 5-10 / 20-25 |
| 70/30 TS | 1 | 10 | 60 / 60 | 100 / 100 |
| 70/30 TS | 2 | 10 | 60 / 60 | 100 / 100 |
| 70/30TP | 1 | 10 | 60 / 60 | 100 /100 |
| 70/30TP | 2 | 10 | 60 / 60 | 100 / 100 |
| 60/40 TS | 1 | 10 | 60 / 60 | 35-40 / 40-45 |
| 60/40 TS | 2 | 10 | 60 / 60 | 15-20 / 20-25 |
| 60/40 TP | 1 | 10 | 60 / 60 | 30-35 / 40-45 |
| 60/40 TP | 2 | 10 | 60 / 60 | 10-15 / 25-30 |

As seen in the Table 7.1 MEK results for TOC 1 substrates are successful with all of the samples except PVdF based binders with 60/40 ratio of PVdF and PMMA. Similar problems with compatibility and curing of the 60/40 ratio binders were observed with TOC 2 samples. Also Polyol A + Melamine, Polyol B + Melamine and Polyol C + Melamine gave failed results. All of the failed results were slightly better with the double cured systems, but still the same binders failed. All of the binder systems lost gloss and coloration during the rubbing, but in this thesis the appearance of the coating was not used as a reference of determining the best possible binder for the TOC substrates.

Problems with the MEK results were as predicted from the line-laboratory test results. The curing problems of the TOC 2 during the line trial were considered to be the reason for the poor MEK results, especially with the melamine crosslinked systems. MEK results for Hiarc (PVdF based coating) on the TOC 2 substrate were successful during the line trials. As poor results were observed with both TOC substrates the reasons for the inadequate curing of the 60/40 ratio PVdF-binders were considered to originate from

the paint itself, not just the unsuccessful curing of the TOC 2. The problems with the 60/40 PVdF / PMMA blend could have resulted in poor adhesion between the TOC and the binder due to compatibility issues, or due to unsuccessful curing of the product. All of the samples were cured with a PMT that was tested to work with traditional substrates; theoretically the curing process should not have caused the problems. With a double curing of the products same problems arose, pointing in the direction of poor compatibility between the layers.

As poor MEK results usually cause poor performance in humidity tests, the 60/40 ratio PVdF based paint systems were dropped from the list of potential binders for the final product. Even though the 60/40 ratio binders with the poor MEK results did not show damage from the humidity during the first 250 h of exposure, with past experience a failure in the test is predicted to happen before the binders that had good MEK results.

## 7.2 Mechanical properties

Mechanical properties were tested to determine the best possible binder, thickness and curing cycle for the final test series. Mechanical properties were valued with a significantly lower importance than the humidity test results. T-bend and impact tests were administered to all of the samples painted in the laboratory. The aim for the mechanical testing was to narrow down the list of potential binder, thickness and curing cycle combinations. The results for TOC 1 and TOC 2 substrates were analyzed separately, in order to determine the best possible combination of parameters for each of the TOCs. All of the test results for the film thickness measures, impact resistance testing and T-bend testing are shown in APPENDIX 1-3.

### 7.2.1 T-bend

T-bend test was performed according to the standard, but the results were analyzed with an accuracy of 0.1 units. The test results showed varying differences between the binders chosen for this thesis. A repeating trend with all of the binders was observed, the most flexible coating system was also the thickest coating system. Only slight changes were observed between single and double curing, therefore a definitive ruling on behalf of either cycle could not be made. With TOC 1 the best results from the T-bend test are shown in Table 7.2, and the best results for TOC 2 substrates in Table 7.3.

***Table 7.2.*** *T-bend results for five of the best TOC 1 coating systems with 5 µm, 10 µm and 15 µm thicknesses*

| TOC 1 Sample (Polyester) | Curing [1x, 2x] | Thickness [µm] | T-bend (flexibility / loss of adhesion) [T] | TOC 1 Sample (PVdF) | Curing [1x, 2x] | Thickness [µm] | T-bend (flexibility / loss of adhesion) [T] |
|---|---|---|---|---|---|---|---|
| C+M | 1 | 15 | 0.7 / 0 | 70/30 TS | 2 | 15 | 0.5 / 0 |
| A+I | 1 | 15 | 0.8 / 0 | 60/40 TP | 1 | 15 | 0.6 / 0 |
| A+M | 2 | 15 | 1.0 / 0 | 70/30 TS | 1 | 15 | 0.7 / 0 |
| B+M | 1 | 15 | 1.2 / 0 | 60/40 TS | 2 | 15 | 0.8 / 0 |
| C+M | 2 | 15 | 1.2 / 0 | 60/40 TS | 1 | 15 | 0.9 / 0 |
| C+M | 1 | 10 | 1.4 / 0 | 60/40 TP | 2 | 10 | 1.1 / 0 |
| A+M | 2 | 10 | 1.4 / 0 | 60/40 TP | 1 | 10 | 1.4 / 0 |
| C+M | 2 | 10 | 1.5 / 0 | 60/40 TS | 2 | 10 | 1.4 / 0 |
| A+I | 1 | 10 | 1.7 / 0 | 70/30 TS | 2 | 10 | 1.5 / 0 |
| B+M | 1 | 10 | 1.7 / 0.2 | 60/40 TS | 1 | 10 | 1.5 / 0 |
| B+M | 2 | 5 | 1.7 / 0.4 | 70/30 TS | 2 | 5 | 1.7 / 0 |
| C+M | 1 | 5 | 1.8 / 0 | 70/30 TS | 1 | 5 | 2.0 / 0.7 |
| B+M | 1 | 5 | 2.2 / 0.9 | 60/40 TS | 2 | 5 | 2.2 / 0 |
| A+M | 1 | 5 | 2.4 / 0 | 60/40 TS | 1 | 5 | 2.4 / 0 |
| C+M | 2 | 5 | 2.4 / 0 | 60/40 TP | 2 | 5 | 2.4 / 0.5 |

***Table 7.3.*** *T-bend results for five of the best TOC 2 coating systems with 5 µm, 10 µm and 15 µm thicknesses*

| TOC 2 Sample (Polyester) | Curing [1x, 2x] | Thickness [µm] | T-bend (flexibility / loss of adhesion) [T] | TOC 2 Sample (PVdF) | Curing [1x, 2x] | Thickness [µm] | T-bend (flexibility / loss of adhesion) [T] |
|---|---|---|---|---|---|---|---|
| A+M | 1 | 15 | 0 / 0 | 60/40 TP | 2 | 15 | 0.1 / 0 |
| B+M | 1 | 15 | 0 / 0 | 70/30 TP | 2 | 15 | 0.4 / 0 |
| B+M | 2 | 15 | 0 / 0 | 70/30 TS | 1 | 15 | 0.4 / 0 |
| C+M | 2 | 15 | 0 / 0 | 60/40 TS | 2 | 15 | 0.5 / 0 |
| C+M | 1 | 15 | 0.5 / 0 | 60/40 TP | 1 | 15 | 0.6 / 0 |
| B+M | 1 | 10 | 0 / 0 | 70/30 TP | 2 | 10 | 1.4 / 0 |
| B+M | 2 | 10 | 0.4 / 0 | 70/30 TP | 1 | 10 | 1.0 / 0 |
| C+M | 2 | 10 | 0.6 / 0 | 70/30 TS | 1 | 10 | 1.2 / 0 |
| A+I | 1 | 10 | 0.9 / 0 | 60/40 TS | 2 | 10 | 1.5 / 0 |
| A+I | 2 | 10 | 1.3 / 0.6 | 60/40 TP | 2 | 10 | 1.5 / 0 |
| B+M | 2 | 5 | 1.5 / 1.3 | 70/30 TP | 1 | 5 | 1.3 / 0 |
| B+M | 1 | 5 | 1.7 / 1.5 | 70/30 TP | 2 | 5 | 1.8 / 0.7 |
| C+M | 2 | 5 | 1.7 / 0 | 70/30 TS | 2 | 5 | 2.6 / 0 |
| A+M | 1 | 5 | 2.1 / 1.5 | 60/40 TP | 2 | 5 | 2.7 / 0.3 |
| A+M | 2 | 5 | 2.5 / 1.6 | 60/40 TP | 1 | 5 | 2.7 / 0.4 |

The results were arranged based on the flexibility values. Adhesion loss was observed mainly on the 5 µm thick samples and was not used as a factor for elimination of the binders. With the above listed results some of the binders could be selected as the best possible alternative based on the flexibility. With TOC 1 substrate the polyester based binders C+M, B+M and PVdF based binders 70/30 TS, 60/40 TP showed best performance. With TOC 2 substrates the same polyester based binders showed promising performance and in case of the PVdF based binders the best results were observed with 70/30 TP and 70/30 TS.

### 7.2.2 Impact resistance

Impact resistance test was administered based on the standard, but modified to ensure more distinctive variations between the results of the samples. All of the samples were

exposed to a set of 160, 140, 120 and 100 lbf in impacts. Each of the impacts was valued between 1 and 5 from the edges of the deformed cup and from the center of the cup. An average value of the above mentioned two observations was calculated for each of the impacts. The final value of the impact test was the sum of all of the four different impacts valued as described above. The impact resistance value for each of the samples was between 4 (flawless) and 20 (severely damaged). Five samples, from each thickness range, with the best impact resistance values are presented in the Table 7.4 and Table 7.5. All binders withstood the adhesion loss test, described in the standard, at 160 lbf in.

***Table 7.4.*** *Impact resistance test results for five of the best TOC 1 coating systems with 5 µm, 10 µm and 15 µm thicknesses*

| TOC 1 Sample (Polyester) | Curing [1x, 2x] | Thickness [µm] | Impact resistance [from 4 to 20] | TOC 1 Sample (PVdF) | Curing [1x, 2x] | Thickness [µm] | Impact resistance [from 4 to 20] |
|---|---|---|---|---|---|---|---|
| B+M | 1 | 15 | 4 | 60/40 TP | 2 | 15 | 4 |
| C+M | 1 | 15 | 4.5 | 70/30 TP | 2 | 15 | 4 |
| B+M | 2 | 15 | 4.5 | 70/30 TP | 2 | 15 | 4.5 |
| C+M | 2 | 15 | 4.5 | 60/40 TP | 1 | 15 | 4.5 |
| A+M | 2 | 15 | 7 | 70/30 TP | 1 | 15 | 4.5 |
| C+M | 2 | 10 | 5.5 | 60/40 TS | 2 | 10 | 4 |
| B+M | 1 | 10 | 6 | 60/40 TP | 2 | 10 | 5.5 |
| B+M | 2 | 10 | 6.5 | 70/30 TS | 2 | 10 | 5.5 |
| A+I | 1 | 10 | 8 | 60/40 TP | 1 | 10 | 5.5 |
| C+M | 1 | 10 | 8.5 | 70/30 TP | 1 | 10 | 5.5 |
| C+M | 1 | 5 | 8.5 | 60/40 TP | 2 | 5 | 8 |
| C+M | 2 | 5 | 8.5 | 60/40 TS | 2 | 5 | 8 |
| B+M | 1 | 5 | 9 | 70/30 TP | 1 | 5 | 8 |
| A+I | 2 | 5 | 9.5 | 70/30 TS | 2 | 5 | 8.5 |
| B+M | 2 | 5 | 9.5 | 60/40 TS | 1 | 5 | 8.5 |

***Table 7.5.*** *Impact resistance test results for five of the best TOC 2 coating systems with 5 µm, 10 µm and 15 µm thicknesses*

| TOC 2 Sample (Polyester) | Curing [1x, 2x] | Thickness [µm] | Impact resistance [from 4 to 20] | TOC 2 Sample (PVdF) | Curing [1x, 2x] | Thickness [µm] | Impact resistance [from 4 to 20] |
|---|---|---|---|---|---|---|---|
| B+M | 1 | 15 | 4 | 60/40 TP | 2 | 15 | 4 |
| B+M | 2 | 15 | 4.5 | 60/40 TS | 1 | 15 | 4 |
| C+M | 1 | 15 | 4.5 | 60/40 TS | 2 | 15 | 4.5 |
| C+M | 2 | 15 | 4.5 | 70/30 TP | 1 | 15 | 4.5 |
| A+M | 1 | 15 | 7 | 70/30 TP | 2 | 15 | 4.5 |
| B+M | 2 | 10 | 5.5 | 70/30 TP | 2 | 10 | 4 |
| B+M | 1 | 10 | 6 | 70/30 TS | 1 | 10 | 5.5 |
| C+M | 1 | 10 | 6.5 | 60/40 TP | 2 | 10 | 5.5 |
| C+M | 2 | 10 | 8 | 60/40 TS | 2 | 10 | 5.5 |
| A+I | 2 | 10 | 8.5 | 60/40 TP | 1 | 10 | 5.5 |
| B+M | 1 | 5 | 8.5 | 70/30 TS | 2 | 5 | 8 |
| C+M | 2 | 5 | 8.5 | 70/30 TS | 1 | 5 | 8 |
| B+M | 2 | 5 | 9 | 60/40 TS | 2 | 5 | 8 |
| C+M | 1 | 5 | 9.5 | 70/30 TP | 2 | 5 | 8.5 |
| A+I | 2 | 5 | 9.5 | 60/40 TP | 2 | 5 | 8.5 |

With the impact resistance test a set of binders could be selected as the ones with best performance against rapid deformation. TOC 1 and TOC 2 substrates with B+M and C+M binders performed with the best results regardless of the thickness of the coating. PVdF based binders 70/30 TP, 60/40 TP and 60/40 TS worked equally well with TOC 1. With TOC 2 substrate PVdF based binders 60/40 TP, 70/30TP and 70/30 TS performed with good results.

### 7.2.3 QCT

All of the 96 samples were exposed to a cycle of 1000 h of QCT testing in a temperature of approximately 60 °C with a relative humidity of 100%. The samples were checked every 250 h and a classification of the damages to the samples were done as

explained in the 6.4.4 Resistance to humidity (QCT). In the Table 7.6 and Table 7.7 the results from the QCT test are shown.

***Table 7.6.*** *QCT test results for TOC 1 samples*

| Sample (Polyester) | Curing [1x, 2x] | Thickness [µm] | TOC 1 | | | | Sample (PVDF) | Curing [1x, 2x] | Thickness [µm] | TOC 1 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 250 h | 500 h | 750 h | 1000 h | | | | 250 h | 500 h | 750 h | 1000 h |
| A+I | 1x | 5 | 3s2 | 4s2 | 4s2 | 4s2 | 60/40 TP | 1x | 5 | 5s2 | 5s2 | 5s2 | 5s2 |
| A+I | 1x | 10 | 4s2 | 4s2 | 4s2 | 4s2 | 60/40 TP | 1x | 10 | 4s2 | 5s2 | 5s2 | 5s2 |
| A+I | 1x | 15 | 4s2 | 5s2 | 5s2 | 5s2 | 60/40 TP | 1x | 15 | 3s2 | 3s2 | 3s2 | 4s2 |
| A+I | 2x | 5 | 3s2 | 3s2 | 3s2 | 3s2 | 60/40 TP | 2x | 5 | 5s2 | 5s2 | 5s2 | 5s2 |
| A+I | 2x | 10 | 3s2 | 3s2 | 3s2 | 3s2 | 60/40 TP | 2x | 10 | 4s2 | 5s2 | 5s2 | 5s2 |
| A+I | 2x | 15 | 4s2 | 4s2 | 4s2 | 4s2 | 60/40 TP | 2x | 15 | 2s2 | 3s2 | 3s2 | 4s2 |
| A+M | 1x | 5 | 4s2 / 5s2 | 5s2 | 5s2 | 5s2 | 60/40 TS | 1x | 5 | 5s2 | 5s2 | 5s2 | 5s2 |
| A+M | 1x | 10 | 4s2 | 5s2 | 5s2 | 5s2 | 60/40 TS | 1x | 10 | 3s2 | 4s2 | 4s2 | 5s2 |
| A+M | 1x | 15 | 5s2 | 5s2 + *s3 | 5s2 + *s3 | 5s2 + *s3 | 60/40 TS | 1x | 15 | 3s2 | 4s2 | 4s2 | 4s2 |
| A+M | 2x | 5 | 4s2 / 5s2 | 5s2 | 5s2 | 5s2 | 60/40 TS | 2x | 5 | 5s2 | 5s2 | 5s2 | 5s2 |
| A+M | 2x | 10 | 4s2 | 5s2 | 5s2 | 5s2 | 60/40 TS | 2x | 10 | 3s2 | 4s2 | 4s2 | 5s2 |
| A+M | 2x | 15 | 4s2 | 5s2 | 5s2 | 5s2 | 60/40 TS | 2x | 15 | 2s2 | 4s2 | 4s2 | 4s2 |
| B+M | 1x | 5 | 5s2 | 5s2 / 3s3 | 5s3 | 5s3 | 70/30 TP | 1x | 5 | 3s2 | 3s2 | 4s2 | 5s2 |
| B+M | 1x | 10 | 2s3 | 5s3 | 5s3 | 5s3 | 70/30 TP | 1x | 10 | 3s2 | 3s2 | 3s2 | 3s2 |
| B+M | 1x | 15 | 5s2 + *s3 | 5s4 | 5s4 | 5s4 | 70/30 TP | 1x | 15 | 2s2 | 2s2 | 2s2 | 2s2 |
| B+M | 2x | 5 | 4s2 | 5s2 | 5s2 | 5s2 | 70/30 TP | 2x | 5 | 3s2 | 3s2 | 4s2 | 4s2 |
| B+M | 2x | 10 | 5s2 + *s3 | 5s3 | 5s3 | 5s3 | 70/30 TP | 2x | 10 | 3s2 | 3s2 | 3s2 | 3s2 |
| B+M | 2x | 15 | 4s3 | 4s4 | 4s4 | 4s4 | 70/30 TP | 2x | 15 | 2s2 | 2s2 | 2s2 | 2s2 |
| C+M | 1x | 5 | 5s2 | 5s2 | 5s2 | 5s2 | 70/30 TS | 1x | 5 | 3s2 | 3s2 | 3s2 | 3s2 |
| C+M | 1x | 10 | 5s2 + *s3 | 5s2 + *s3 | 5s2 + *s3 | 5s2 + *s3 | 70/30 TS | 1x | 10 | 2s2 | 2s2 | 2s2 | 2s2 |
| C+M | 1x | 15 | 5s2 | 5s2 | 5s2 | 5s2 | 70/30 TS | 1x | 15 | 0 | 0 | 0 | 0 |
| C+M | 2x | 5 | 5s2 | 5s2 | 5s2 | 5s2 | 70/30 TS | 2x | 5 | 3s2 | 3s2 | 4s2 | 4s2 |
| C+M | 2x | 10 | 5s2 / 4s2 | 5s2 | 5s2 | 5s2 | 70/30 TS | 2x | 10 | 0 | 0 | 0 | 0 |
| C+M | 2x | 15 | 4s2 | 5s2 | 5s2 | 5s2 | 70/30 TS | 2x | 15 | 0 | 0 | 0 | 0 |

* singular spot with the corresponding damage

***Table 7.7.*** *QCT test results for TOC 2 samples*

| Sample (Polyester) | Curing [1x, 2x] | Thickness [µm] | TOC 2 250 h | 500 h | 750 h | 1000 h |
|---|---|---|---|---|---|---|
| A+I | 1x | 5 | 0 | 0 | 0 | 0 |
| A+I | 1x | 10 | 0 | 0 | 0 | 0 |
| A+I | 1x | 15 | 0 | 0 | 0 | 0 |
| A+I | 2x | 5 | 0 | 0 | 0 | 0 |
| A+I | 2x | 10 | 0 | 0 | 0 | 0 |
| A+I | 2x | 15 | 0 | 0 | 0 | 0 |
| A+M | 1x | 5 | X | x | | |
| A+M | 1x | 10 | X + ** 5s3 | x | | |
| A+M | 1x | 15 | 5s3, 2s5 | x | POISTETTU | |
| A+M | 2x | 5 | X | x | KAAPISTA | |
| A+M | 2x | 10 | 5s3, 2s4 | x | | |
| A+M | 2x | 15 | 5s2, 4s3 | x | | |
| B+M | 1x | 5 | X | x | | |
| B+M | 1x | 10 | 3s5, 5s3 | x | | |
| B+M | 1x | 15 | 0 + ** 4s3 | 5s3, 2s5 | POISTETTU | |
| B+M | 2x | 5 | X | x | KAAPISTA | |
| B+M | 2x | 10 | 0 | x | | |
| B+M | 2x | 15 | 0 | 5s3 | | |
| C+M | 1x | 5 | 4s4, 2s5 | x | | |
| C+M | 1x | 10 | 4s5 | x | | |
| C+M | 1x | 15 | 5s3 | 5s4 | POISTETTU | |
| C+M | 2x | 5 | 4s3 | x | KAAPISTA | |
| C+M | 2x | 10 | 3s2, 3s3 | x | | |
| C+M | 2x | 15 | 3s2, 4s2 | 5s4 | | |

| Sample (PVDF) | Curing [1x, 2x] | Thickness [µm] | TOC 2 250 h | 500 h | 750 h | 1000 h |
|---|---|---|---|---|---|---|
| 60/40 TP | 1x | 5 | 0 + * s2 | 2s2 | 2s2 | 3s2 |
| 60/40 TP | 1x | 10 | 0 | 0 | 2s2 | 3s2 |
| 60/40 TP | 1x | 15 | 0 | 0 | 2s2 | 3s2 |
| 60/40 TP | 2x | 5 | 0 | 0 | 2s2 | 2s2 |
| 60/40 TP | 2x | 10 | 0 | 0 | 2s2 | 3s2 |
| 60/40 TP | 2x | 15 | 0 | 0 | 2s2 | 2s2 |
| 60/40 TS | 1x | 5 | 0 + * s2 | 2s2 | 4s2 | 5s2 |
| 60/40 TS | 1x | 10 | 0 | 3s2 | 3s2 | 4s2 |
| 60/40 TS | 1x | 15 | 0 | 0 | 3s2 | 3s2 |
| 60/40 TS | 2x | 5 | 0 | 0 | 3s2 | 3s3 |
| 60/40 TS | 2x | 10 | 0 | 0 | 2s2 | 2s3 |
| 60/40 TS | 2x | 15 | 0 + * s2 | 3s2 | 3s2 | 3s2 |
| 70/30 TP | 1x | 5 | 0 | 0 | 0 | 0 |
| 70/30 TP | 1x | 10 | 0 | 0 | 0 | 0 |
| 70/30 TP | 1x | 15 | 0 + ** 3s2 | 0 + ** 3s2 | 0 + ** 3s2 | 0 + ** 3s2 |
| 70/30 TP | 2x | 5 | 0 | 0 | 0 | 0 |
| 70/30 TP | 2x | 10 | 0 | 0 | 0 | 0 |
| 70/30 TP | 2x | 15 | 0 | 0 | 0 | 0 |
| 70/30 TS | 1x | 5 | 0 | 0 | 2s2 | 2s2 |
| 70/30 TS | 1x | 10 | 0 + *s2 | 0 + *s2 | 3s2 | 5s2 |
| 70/30 TS | 1x | 15 | 0 + ** 2s4 | 0 + ** 2s4 | 3s2 + ** 2s4 | 3s2 + **2s4 |
| 70/30 TS | 2x | 5 | 0 + *s2 | 0 + *s2 | 3s2 | 3s3 |
| 70/30 TS | 2x | 10 | 0 | 0 | 2s2 | 4s2 |
| 70/30 TS | 2x | 15 | 0 | 0 | 3s2 | 4s2 + *s5 |

* singular spot with the corresponding damage, ** a clear stain with corresponding damage

The results of the QCT were quite apparent already from the 250 h mark, with some of the samples severely damaged and others barely showing any signs of deterioration. After the 500 h mark the samples for further analysis were selected. A selection of the most promising binders, from both the PVDF and polyester based binder categories, for both TOC substrates was selected. As seen in the Figure 7.1 the level of deterioration ruled out several binders, the remaining binders were analyzed with the ANOVA-method.


***Figure 7.1.*** *Example of different levels of deterioration amongst the samples*

TOC 1 substrate showed promising results with a variety of binders in both the polyester and PVdF based binders. Polyol A + I and polyol C + M were selected from the polyester based binders and 70/30 TS and 70/30 TP were selected from the PVdF based binders. TOC 2 substrate performed as expected and only the Polyol A + I withstood the humidity from the polyester based binders. As with the PVDF based binders, all showed promising, but as explained in the subchapter 7.1 Compatibility between the binders and the TOCs the 60/40 ratio binders were not selected for further testing due to the inferior MEK results.

A similar trend with the film thickness was observed from the QCT results as was observed from the mechanical results. The most promising film thickness appears to be the 15 µm thick version. The curing cycles with single or double curing did not seem to make a significant difference to the QCT results. All of the QCT results can be found in APPENDIX 4.

## 7.3 ANOVA

As explained earlier in the subchapter 6.5 Statistical analysis (ANOVA) the choices for the final products were made with a collaboration of QCT results, interpreted individually for each binder, and with a statistical analysis of the mechanical properties, done with ANOVA. The QCT results narrowed down the most potential binders based on the humidity resistance properties, which were graded to be the most vital property in this thesis. Statistical analysis was used not only to choose the best performing binder from the most potential binders but also to determine the other properties of the final product. With ANOVA the best combination of binder, film thickness and curing cycle was predicted. The results from ANOVA are presented and explained in this subchapter.

### 7.3.1 Binder

From the earlier results (QCT) a set of binders were selected for further study. With TOC 1 substrate the QCT results narrowed the choice of the polyester based binder to A+I or C+M and PVdF based binders to 70/30 TP or 70/30 TS. As for TOC 2 substrate the most potential binders were A+I (others were completely destroyed by the QCT) for polyester based binders and 70/30 TP or 70/30 TS for PVdF based binders. With ANOVA the mechanical testing data was analyzed. With the following figures the choice between the said binders was made and explained.

With TOC 1 the above mentioned binders were analyzed and compared in order to choose the best possible binder for the TOC 1 substrate. As seen in Figure 7.2 the analysis gave results that clearly point out three (color-coded) groups that have significantly different marginal of means, meaning that the results can be compared between the color-coded groups. A+I and C+M are part of different color-coded groups and with a significantly better results (smaller value in impact resistance is better) the C+M (blue group) is a superior choice between A+I and C+M when categorized by impact resistance. In the case of PVdF based binders a clear statistical interpretation of the superiority of the binders could not be made. 70/30 TP and 70/30 TS are statistically considered to be equal based on the impact resistance results.

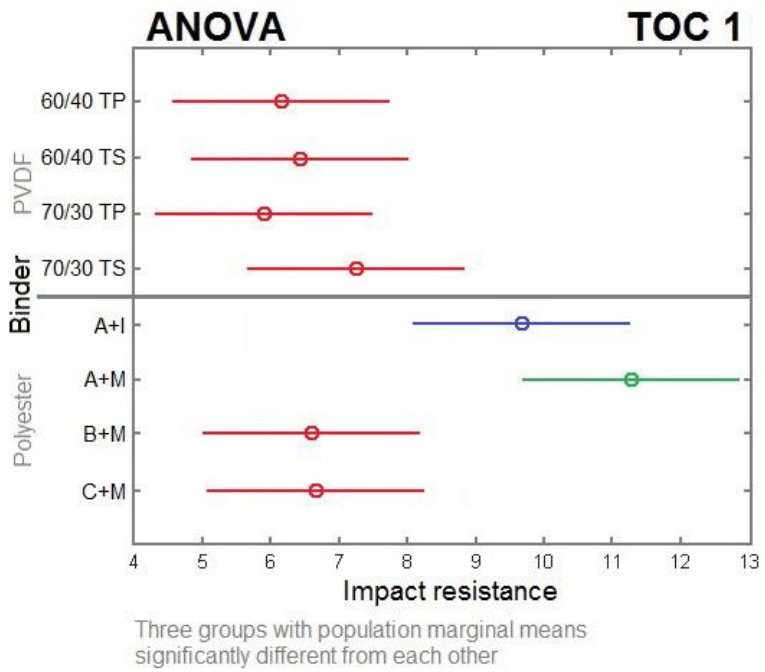


***Figure 7.2.*** *TOC 1 analysis of variance between the binders based on impact resistance results (Three separate color-coded groups with significantly different marginal means)*

The above mentioned binders were analyzed and categorized also by T-bend results. In Figure 7.3 the choice between A+I or C+M and 70/30 TP or 70/30 TS becomes clear. As with the impact resistance results, also with the T-bend results, the choice of C+M over A+I is obvious. With significantly better results in both mechanical properties the C+M was chosen for the final product as the binder choice from the polyester based binders. In the PVDF based category a notable difference was observed on behalf of 70/30 TS.

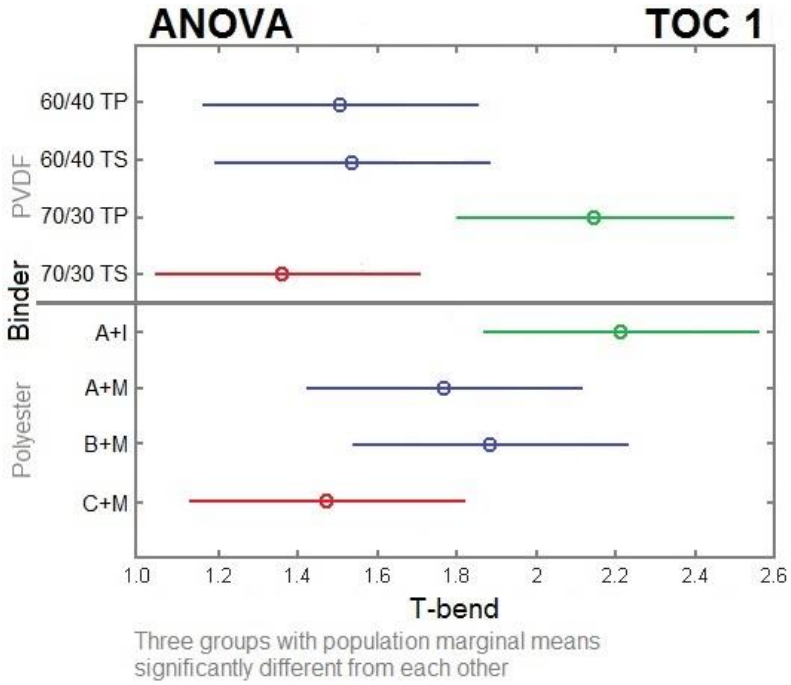

***Figure 7.3.*** *TOC 1 analysis of variance between the binders based on T-bend results (Three separate color-coded groups with significantly different marginal means)*

With these results the choices for the final **TOC 1** product were **C+M** and **70/30 TS**.

TOC 2 substrate was exposed to similar testing and analyzed in the same manner as TOC 1. As seen in Figure 7.4 and Figure 7.5 the PVdF binders could not be categorized based on impact resistance, but the T-bend results reveal the superiority of the 70/30 TP binder.

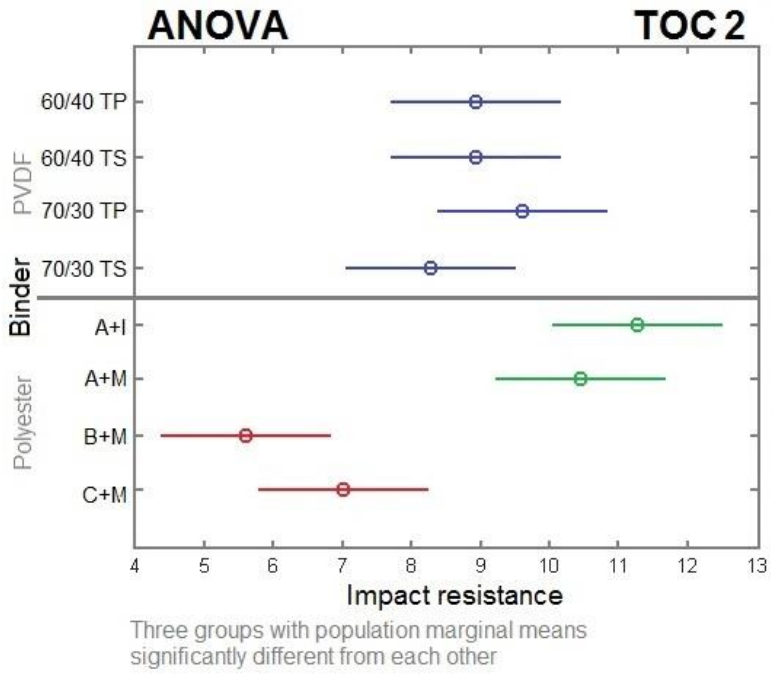


***Figure 7.4.*** *TOC 2 analysis of variance between the binders based on impact resistance results (Three separate color-coded groups with significantly different marginal means)*

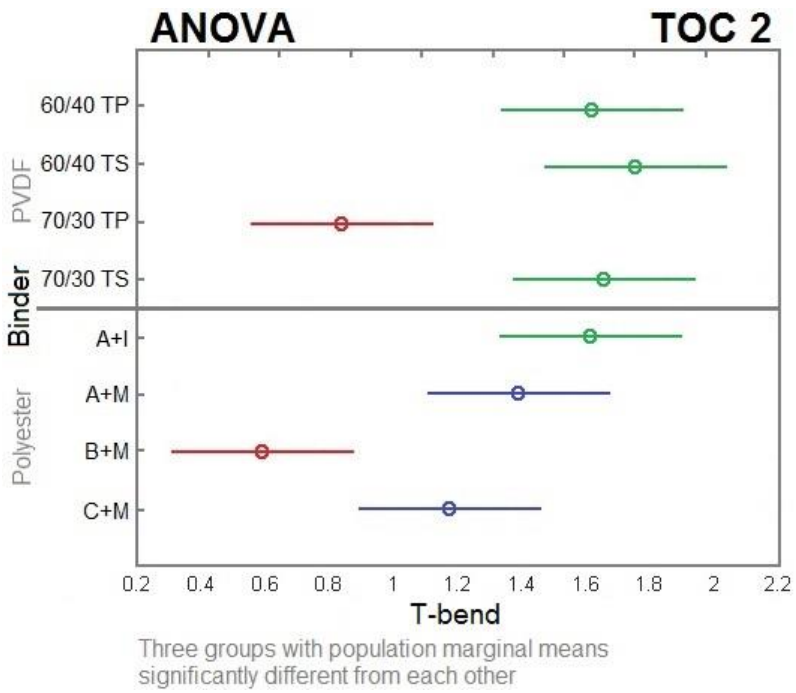


***Figure 7.5.*** *TOC 2 analysis of variance between the binders based on T-bend results (Three separate color-coded groups with significantly different marginal means)*

Even though the superiority of B+M, C+M and A+M binders in mechanical properties becomes obvious from the statistical analysis, based on the QCT results these binders were distinctly inferior in humidity resistance. Humidity resistance was graded the governing attribute for the choice of the binder so the results from ANOVA were ignored in this case. With these results the choices for the final **TOC 2** product were **A+I** and **70/30 TP**.

ANOVA results were plotted to the following figures based on the combination of the T-bend and impact resistance results. The above mentioned selections of binders can be seen from the figures, which represent approximately 68 % of the data spectrum of the results for the specific binder. The mean values mentioned and illustrated in the figures above determine the selection. The following plotted spherical representations are given in this thesis to support the previously stated interpretation of the analysis.

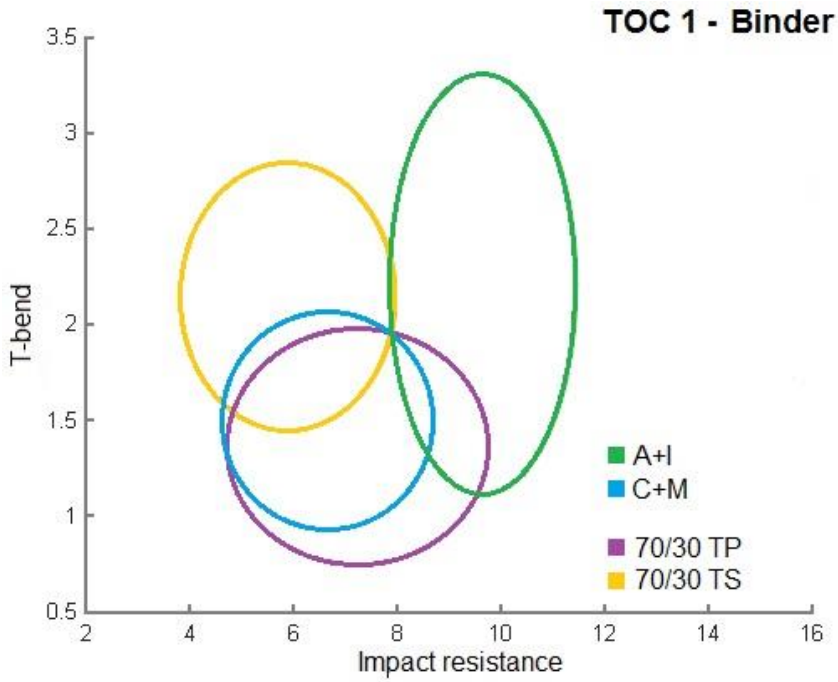


***Figure 7.6.*** *ANOVA results plotted for TOC 1 based on T-bend and impact resistance results*

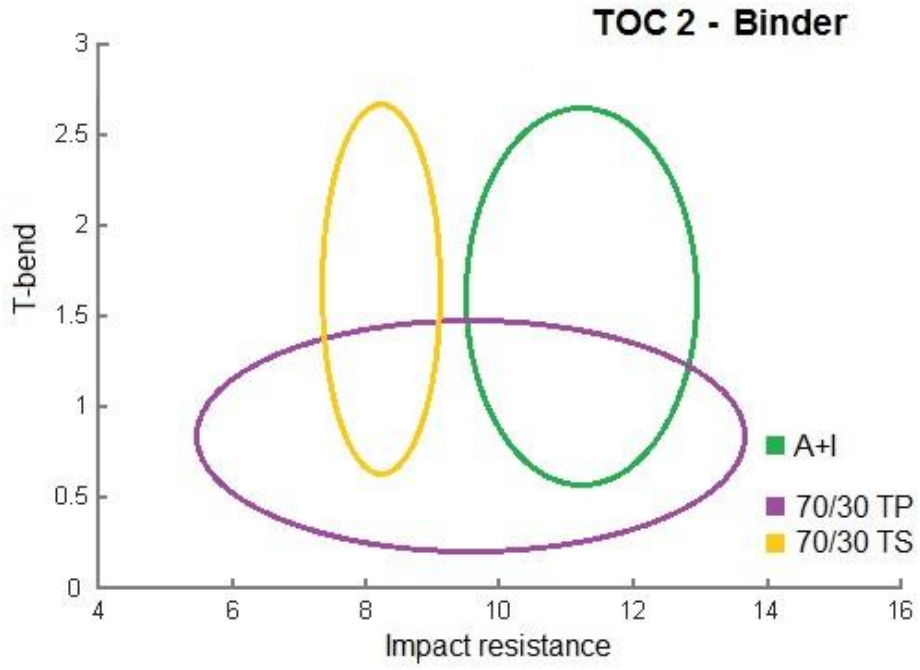


***Figure 7.7.*** *ANOVA results plotted for TOC 2 based on T-bend and impact resistance results*

### 7.3.2 Film thickness

QCT results showed that the best resistance towards exposure to humidity comes from the thickest dry film, regardless of the binder. Statistical analysis was made to determine, if similar results could be obtained from the mechanical resistance testing data. ANOVA-method gave clear and statistically significant prove towards the above mentioned observation from the QCT testing. In the following figures (Figure 7.8 and Figure 7.9) the results from the ANOVA-method are illustrated. As seen from each of the figures all of the film thicknesses used in this thesis were significantly different in terms of marginal means, which again prove that the thickness is a governing factor on the mechanical properties. Similar observations were made from the impact resistance and the T-bend test data.

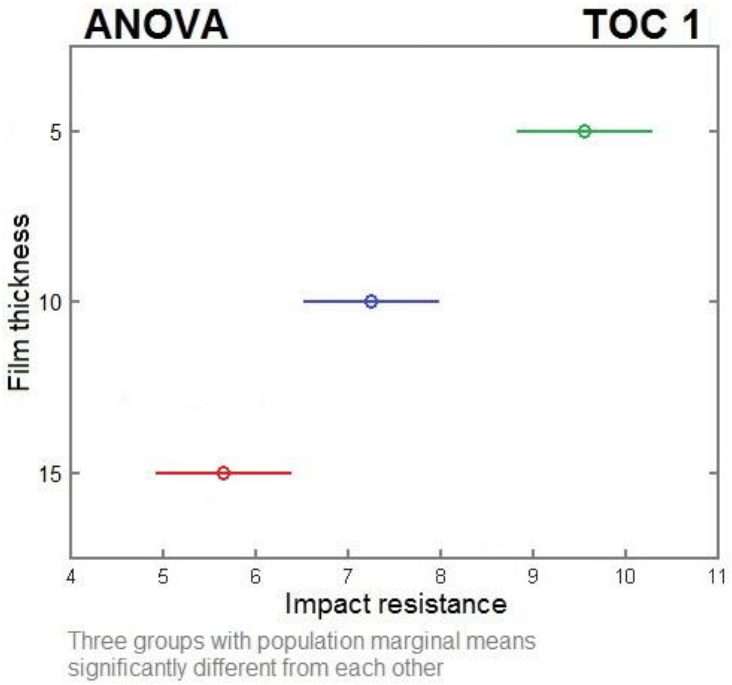


***Figure 7.8.*** *TOC 1(similar results with TOC 2) analysis of variance between the film thicknesses based on impact resistance results (Three separate color-coded groups with significantly different marginal means)*

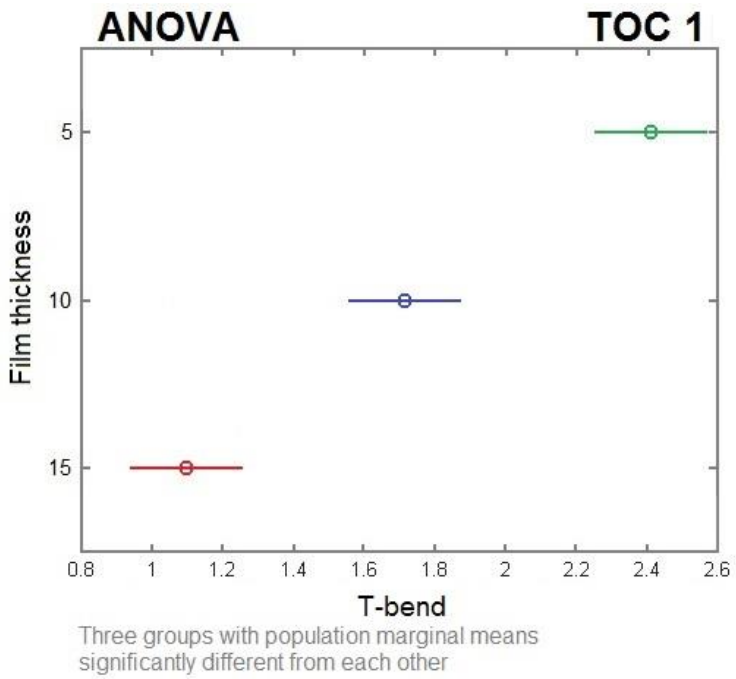


***Figure 7.9*** *TOC 1 (similar results with TOC 2) analysis of variance between the film thicknesses based on T-bend results (Three separate color-coded groups with significantly different marginal means)*

The mechanical properties from both of the substrates increase when the film thickness grows. For optimal properties for the final product a choice of **15 µm** film thickness was made. In the figures below a spherical plotting of the data was made to further demonstrate the clear differences in mechanical properties with different film thicknesses.

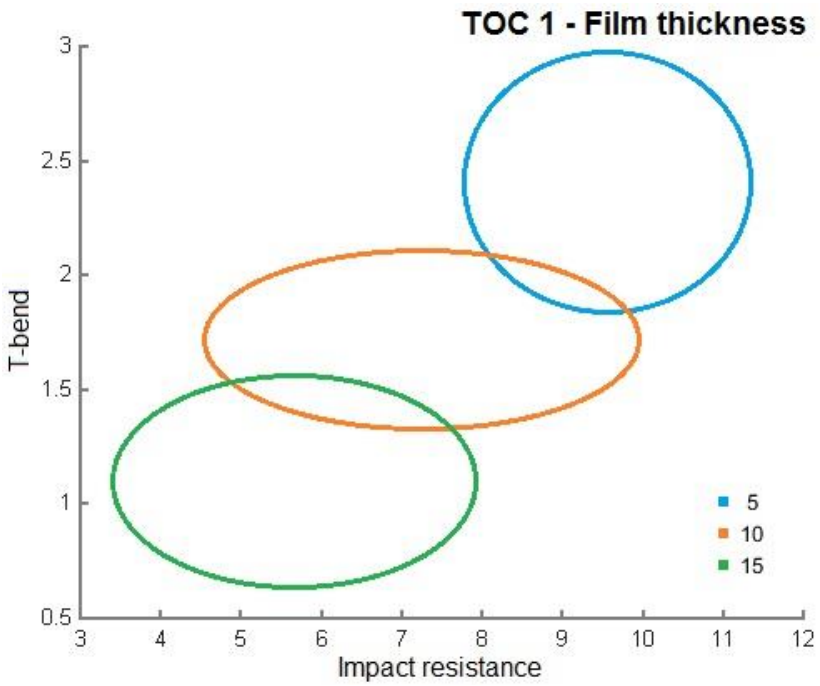


***Figure 7.10.*** *ANOVA results of the film thicknesses plotted for TOC 1(similar results with TOC 2) based on T-bend and impact resistance results*

### 7.3.3 Curing

For the optimal results in the final product the curing cycle was also studied. As one of the variables for the coating systems in this thesis, the data from the mechanical testing was also analyzed from the perspective of the number of curing cycles used. Similar figures as in the previous subchapters were plotted. The only statistically significant difference in the curing cycles was observed with the TOC 2 substrate, when the analysis was based on the impact resistance results. The difference in the curing is illustrated in Figure 7.11.

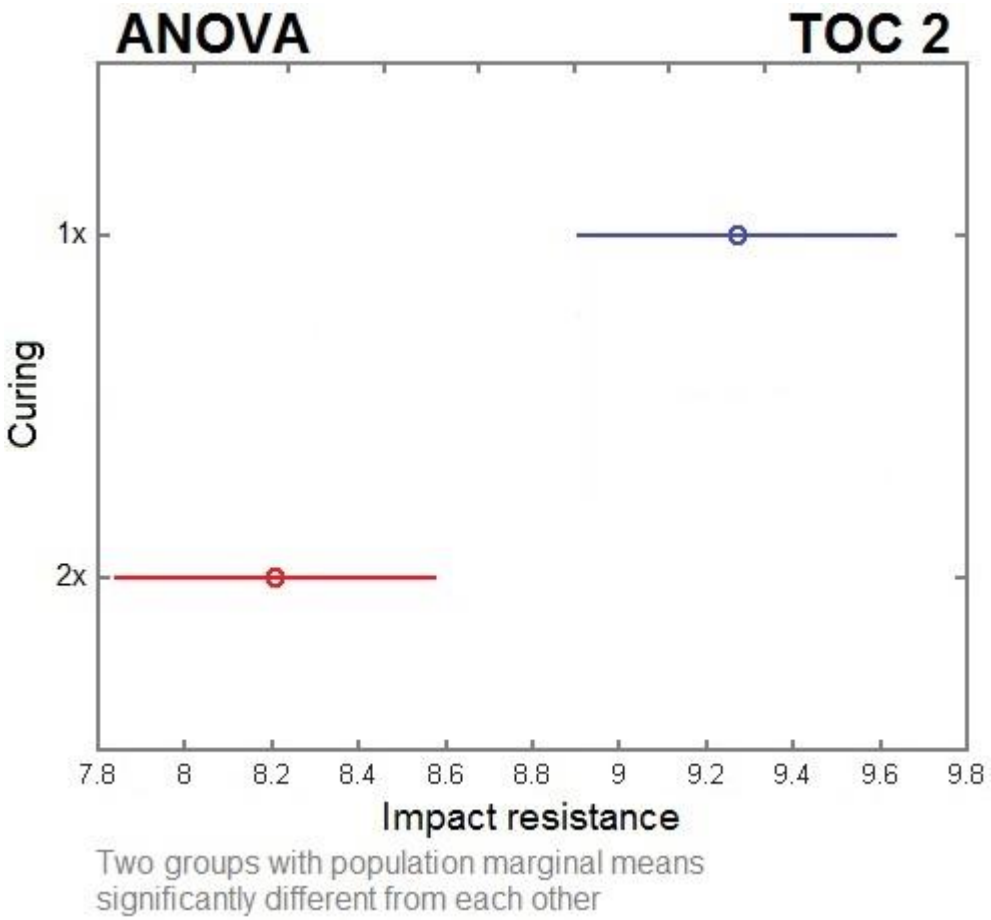


***Figure 7.11.*** *TOC 2 analysis of variance between the curing cycles based on impact resistance results (Two separate color-coded groups with significantly different marginal means)*

The clear difference with TOC 2 substrates mechanical properties based on the curing cycles can be seen from the spherically plotted data from the ANOVA analysis. Illustration of the difference can be seen from the impact resistance results on the x-axis in Figure 7.12.

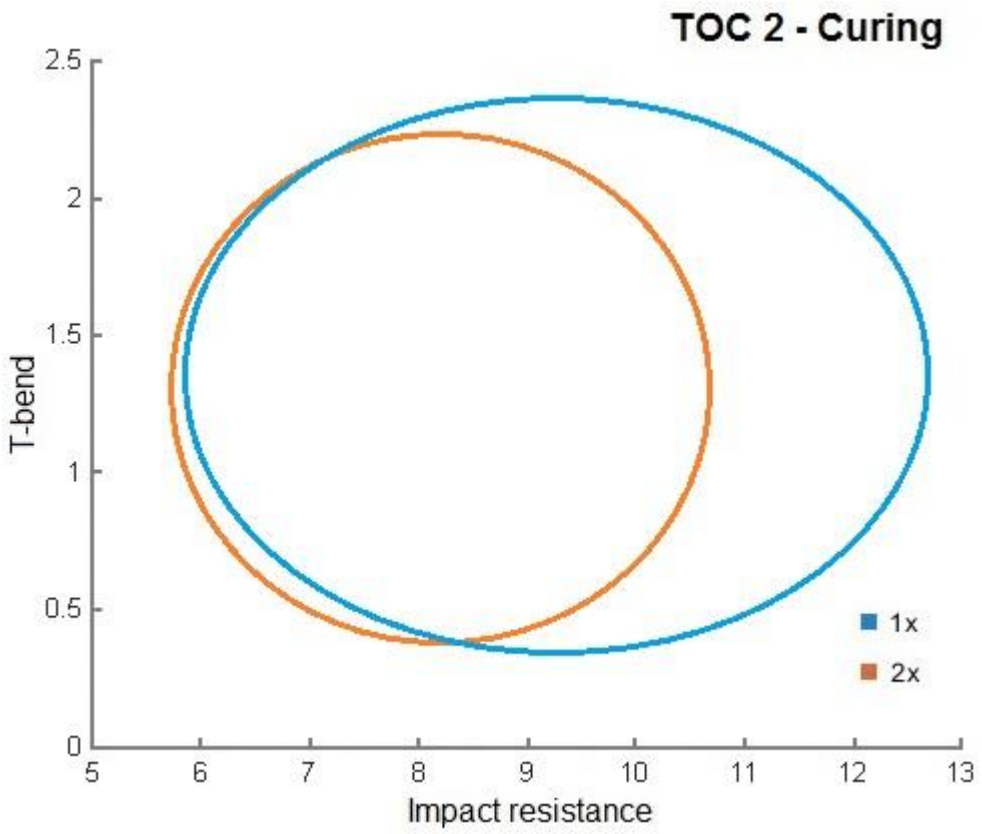


***Figure 7.12.*** *ANOVA results of the curing cycles plotted for TOC 2 based on T-bend and impact resistance results*

As only TOC 2 was affected by the differences in the curing cycles, a choice for the final product was made on behalf of the **double curing** when **TOC 2** substrate is used. With TOC 1 substrate a significant difference between the curing cycles was not observed, therefore a **single curing** was chosen for the **TOC 1** substrate.

## 7.4 Test results from the second test set

Similar test methods that were used with the first sample series were also used to determine the importance of the TOC layer and the pretreatment layer. A comparison between the results from HDG, pretreatment and TOC substrates is presented in this subchapter. All of the results can be found from APPENDIX 5.

### 7.4.1 QCT

A similar QCT cycle was administrated also to the second set of samples, which included the reference samples. A noteworthy trend was observed immediately after the first 250 h interval of exposure. The reference samples with no pretreatment (HDG) started to deteriorate immediately and showed notable blistering only after 250 h of exposure. The blistering for the HDG samples continued with each 250 h interval reaching up to

5(S4). In Figure 7.13, Figure 7.14, Figure 7.15 and Figure 7.16 the results from the humidity exposure are shown after 1000 h of exposure.

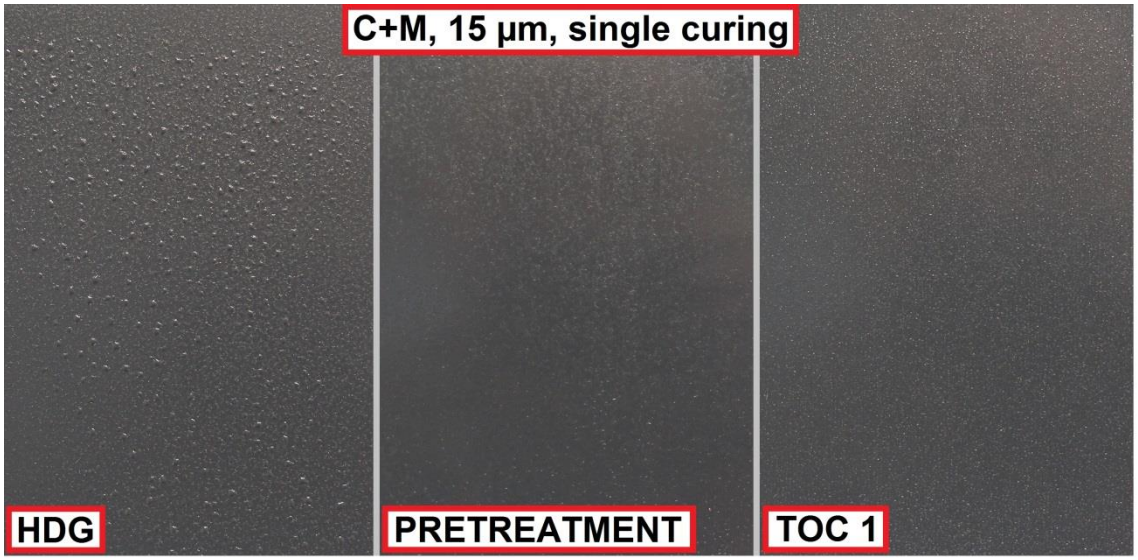


***Figure 7.13.*** *QCT (60 °C, 1000 h) results for C+M binder*

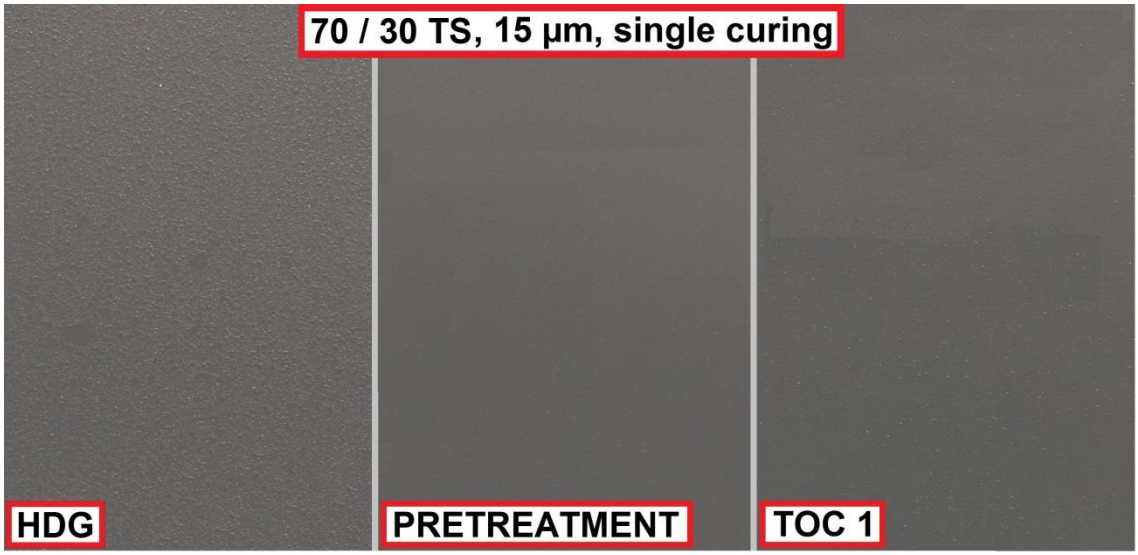


***Figure 7.14.*** *QCT (60 °C, 1000 h) results for 70/30 TS binder*

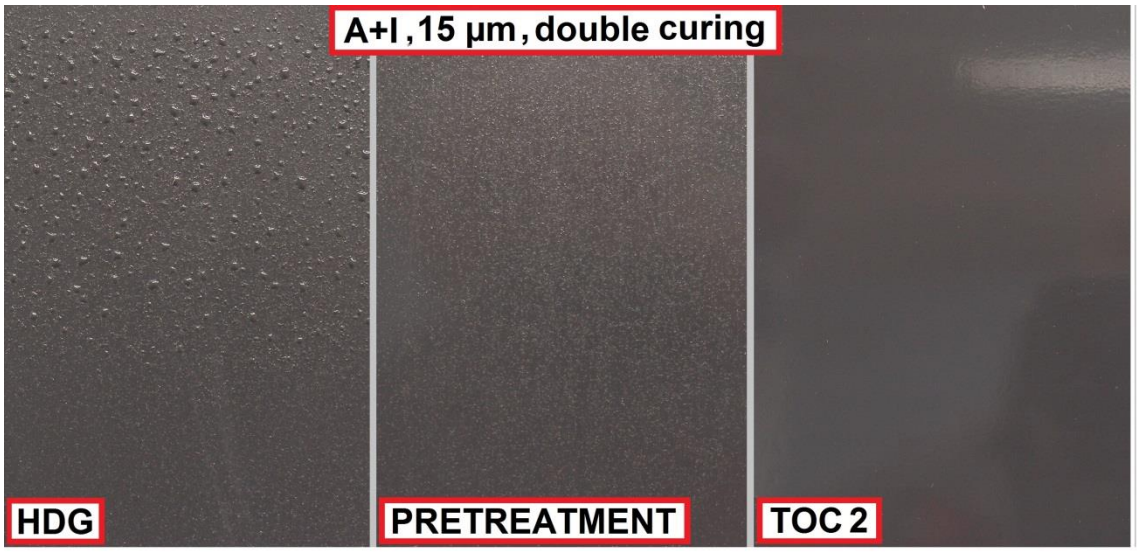


***Figure 7.15.*** *QCT (60 °C, 1000 h) results for A+I binder*

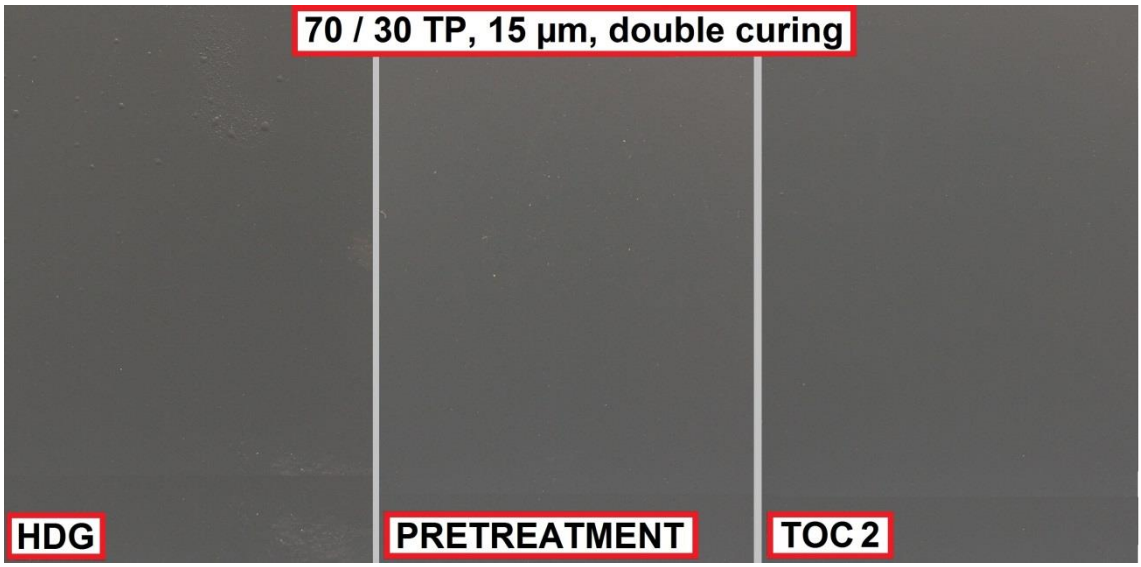


***Figure 7.16.*** *QCT (60 °C, 1000 h) results for 70/30 TP binder*

The traditionally pretreated steel samples deteriorated significantly less than the ones with no pretreatment, as seen in the figures above. With the pretreatment the deterioration after exposure was quite high with A+I binder and some blistering was found also on the C+M binder. With PVdF based binders only singular s2 sized blister was observed, probably due to some stain on the coating.

TOC based samples showed similar blistering than traditional pretreatment with C+M binder, other samples were undamaged. In Table 7.8 the QCT results are shown.

***Table 7.8.*** *QCT results from the second set of samples*

| Substrate | Binder | Curing [1x, 2x] | Thickness [µm] | 250 h | 500 h | 750 h | 1000 h |
|---|---|---|---|---|---|---|---|
| TOC 1 | C+M | 1x | 15 | 3s2 | 4s2 | 5s2 | 5s2 |
| Pretreatment | C+M | 1x | 15 | 4s2 | 5s2 | 5s2 | 5s2 |
| HDG | C+M | 1x | 15 | 5s2 / 4s3 | 4s3 | 3s4 | 5s4 |
| TOC 1 | 70/30 TS | 1x | 15 | 0 | 0 | 2s2 | 3s2 |
| Pretreatment | 70/30 TS | 1x | 15 | 0 + * s2 | 2s2 | 2s2 | 2s2 |
| HDG | 70/30 TS | 1x | 15 | 4s3 | 5s3 + *s4 | 3s4 | 5s4 |
| TOC 2 | A+I | 2x | 15 | 0 | 0 | 0 | 0 |
| Pretreatment | A+I | 2x | 15 | 4s2 | 5s2 | 5s2 | 5s2 |
| HDG | A+I | 2x | 15 | 5s2 / 2s3 | 4s3 | 4s3 | 5s3 / 5s4 |
| TOC 2 | 70/30 TP | 2x | 15 | 0 | 0 | 0 | 2s2 |
| Pre-treatment | 70/30 TP | 2x | 15 | 0 + * s2 | 2s2 | 2s2 | 2s2 |
| HDG | 70/30 TP | 2x | 15 | 2s2 + **5s2 | 3s2 + **3s3 | 3s2+ **3s3 | 3s3 |

* singular spot with the corresponding damage ** a clear stain with corresponding damage

** a clear stain with corresponding damage

Wet/dry adhesion properties were significantly better with the pretreated and thin organic coated samples than with the HDG samples. A severe delamination of the paint occurred with HDG samples as seen in Figure 7.17, Figure 7.18, Figure 7.19 and Figure 7.20.

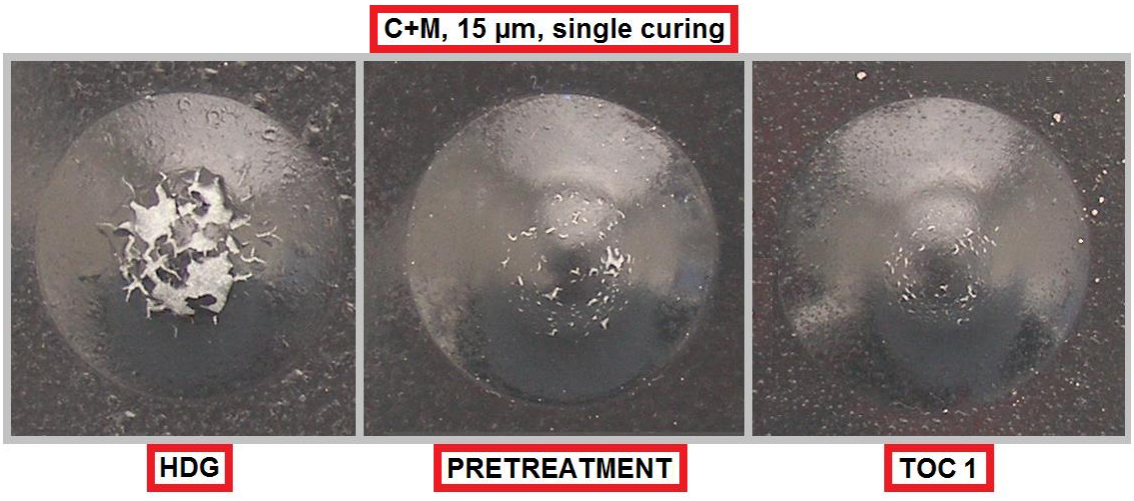


***Figure 7.17.*** *Wet adhesion test results for C+M binder (reverse impact 160 lbf in)*

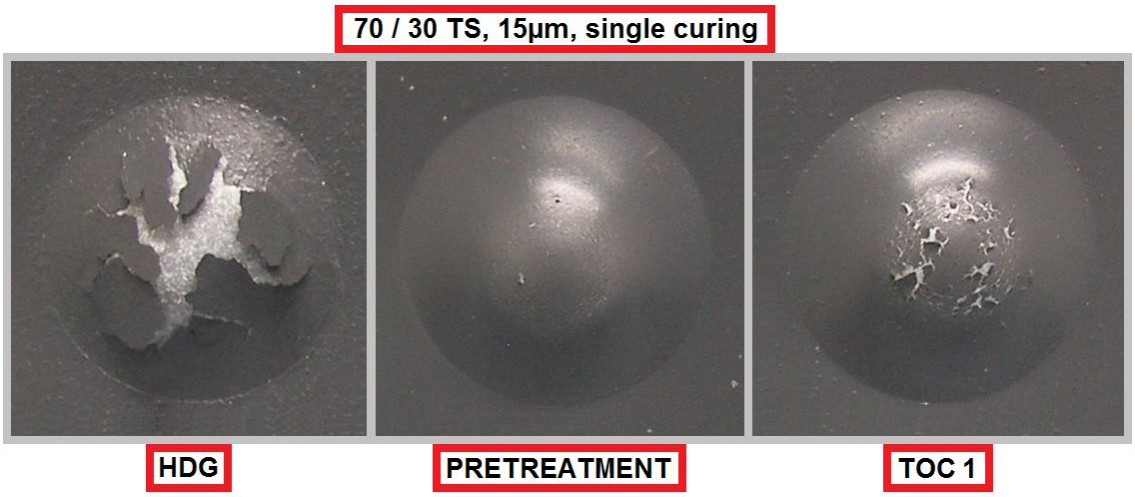


***Figure 7.18.*** *Wet adhesion test results for 70/30 TS binder (reverse impact 160 lbf in)*

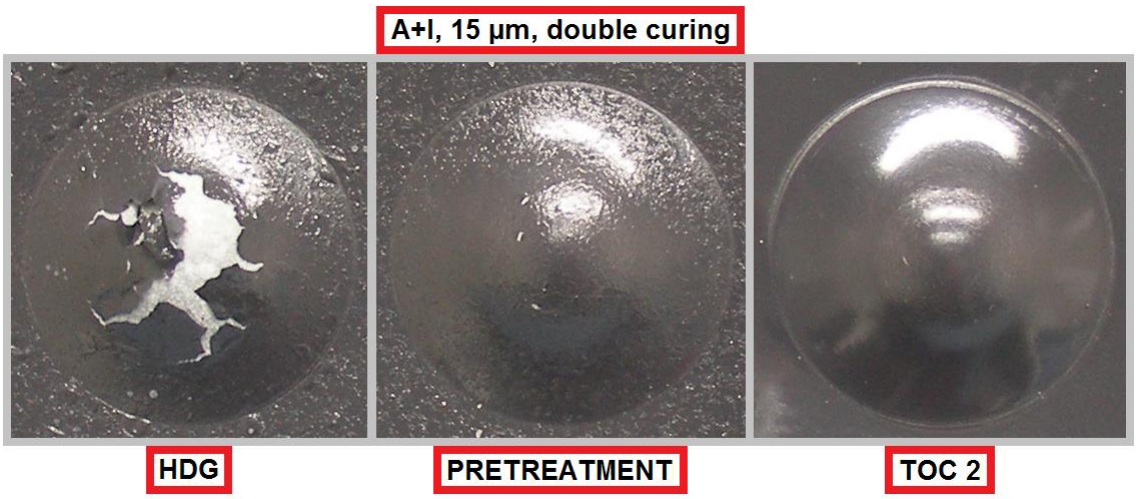


***Figure 7.19.*** *Wet adhesion test results for A+I binder (reverse impact 160 lbf in)*

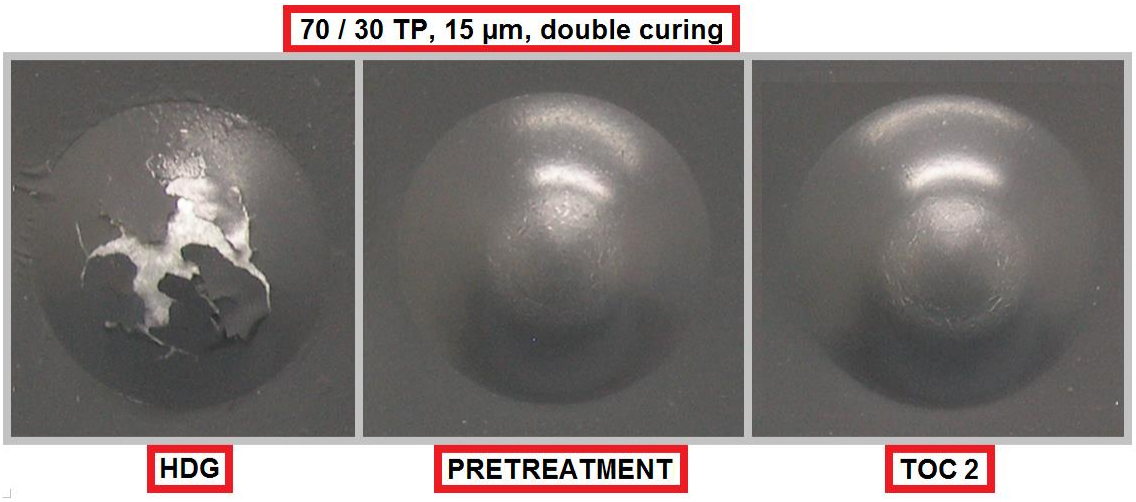


***Figure 7.20.*** *Wet adhesion test results for 70/30 TP binder (reverse impact 160 lbf in)*

TOC 2 performed at least as well as the traditionally pretreated sample. With TOC 1 samples the wet/dry adhesion properties were noticeably inferior to the pretreated samples, especially with the PVdF based 70/30 TS sample. Similar wet/dry adhesion properties were observed with the line trial samples that were studied separately. The manufacturer of TOC 1 started a project to better the above mentioned properties.

### 7.4.2 Mechanical properties

Mechanical testing did not show as clear difference between the HDG, pretreatment and TOC substrates as humidity testing, but a notable trend was observed. C+M binder showed no signs of failure during T-bend test with none of the substrates. A notable difference with C+M binder was observed during the impact resistance testing as the HDG sample showed clear damage from the 160 and 140 lbf in impacts. With traditional pretreatment and TOC 1 based sample only barely visible (10x magnification) damage was observed with the impact of 160 lbf in.

PVdF sample70/30 TS showed some cracking during the T-bend test, resulting in T-values of 2.2 T (HDG), 1.3 T (pretreatment) and 0.4 T (TOC 1). Impact resistance revealed a similar trend in results as the HDG sample showed significant damage from 160, 140, 120 and 100 lbf in impacts. Pretreated sample showed visible damage from 160, 140 and barely visible damage 120 lbf in impacts. The TOC 1 sample with 70/30 TS binder showed only barely visible damage from the 160 lbf in impact and remained undamaged with lesser impacts.

T-bend testing with A+I binder showed some cracking with all of the substrates, resulting in T-values of 0.8 T (HDG), 0.4 T (pretreatment) and 0.3 T (TOC 2). Impact resistance results were similar with all of the substrates resulting in visible damage from 160 and 140 lbf in impacts and barely visible damage from 120 lbf in impact.

PVdf sample 70/30 TP suffered no cracking with T-bend in case of the TOC 2 substrate, but resulted in T-values of 0.5 T (HDG) and 0.2 T (pretreatment) in other substrates. Impact resistance showed once again a distinctive difference between the HDG sample and the other samples. HDG showed significant damage from 160 and 140 lbf in impacts and barely visible damage from 120 lbf in impact. Pretreated and TOC 2 based samples withstood 160 lbf in impact with barely visible damage and suffered no damage from lesser impacts.

None of the samples showed any signs of loss of adhesion, as tested with the adhesion tape after deformation. In the following Table 7.9 the results from mechanical testing are shown with numerical values.

***Table 7.9.*** *Mechanical testing results from the second set of samples*

| Substrate | Binder | Curing [1x, 2x] | Thickness [µm] | T-Bend (flexibility / loss of adhesion) [T] | Impact resistance [from 4 to 20] |
|---|---|---|---|---|---|
| TOC 1 | C+M | 1x | 15 | 0 / 0 | 4 |
| Pretreatment | C+M | 1x | 15 | 0 / 0 | 5 |
| HDG | C+M | 1x | 15 | 0 / 0 | 7 |
| TOC 1 | 70/30 TS | 1x | 15 | 0.4 / 0 | 4.5 |
| Pretreatment | 70/30 TS | 1x | 15 | 1.3 / 0 | 8 |
| HDG | 70/30 TS | 1x | 15 | 2.2 / 0 | 11.5 |
| TOC 2 | A+I | 2x | 15 | 0.8 / 0 | 6.5 |
| Pretreatment | A+I | 2x | 15 | 0.4 / 0 | 6 |
| HDG | A+I | 2x | 15 | 0.3 / 0 | 6 |
| TOC 2 | 70/30 TP | 2x | 15 | 0 / 0 | 4.5 |
| Pretreatment | 70/30 TP | 2x | 15 | 0.2 / 0 | 4.5 |
| HDG | 70/30 TP | 2x | 15 | 0.5 / 0 | 9 |

The mechanical testing data and QCT testing data showed a similar trend in the superiority of the substrates. As predicted with the plain HDG substrate the exposure to humidity results were inferior compared to the other substrates. Mechanical properties revealed similar results from T-bend and impact testing.

With the gathered mechanical testing and QCT testing results it can be observed that the TOC as a replacement for traditional pretreatment and primer keeps the measured properties at similar level. In some cases the TOC performs even better than the traditional system. TOC showed exceptional promise with the humidity resistance results and performed notably better than the traditional system.

# 8. RELIABILITY OF THE RESULTS

In this thesis the emphasis of the experimental part was on the adhesion and interaction between the TOC substrates and the first layer of coating. With a sample set of 96 different binder systems only a fairly limited amount of different tests were performed. The results from the testing could be considered a guideline towards the conclusions and the potential factors for errors in the results should be considered carefully. In this chapter the most probable factors to affect the reliability of the results are discussed.

## 8.1 Error due to the line trials

The substrates (TOCs) for this thesis were received directly from the line trials. The uniformity of the quality of the substrate materials throughout the samples was considered to be on high level. As for the quality of the TOC coating itself, a distribution of the TOC 1 layer was measured to have quite significant variations throughout the width of the coil. Although the average distribution seems to have been in a desired range and the test results of the line run coatings seem to have been consistently good, the poor distribution should be considered as a possibility for inconsistencies in the results.

With TOC 2 substrate the seemingly low PMT during the line trial left the TOC under-cured, resulting most probably in trapped humidity in the coating system. The under-curing of the TOC 2 was studied separately by Top Analytica and the manufacturer of the TOC 2 coating. Results from the separate tests showed a clear under-curing of the TOC 2, but the poor MEK results with polyester based products continued to appear, even with properly cured TOC 2 substrates. Although properly cured TOC 2 substrate showed similar results as the under-cured version, under-curing should be considered as a factor for possible inconsistencies in the results.

An observation of the compatibility of the TOC 2 and polyester based binders was made during the testing of the samples. The incompatibility between the TOC and the binder was discussed to have been caused by the strong alkalinity of the TOC 2 coating and the fact that an acid catalysis is required to properly cure polyester based coatings. The alkaline surface likely disturbed the curing process by acid catalysis. A separate study concerning the phenomena is highly recommended.

## 8.2 Error due to painting process

All of the samples were laboratory painted and cured with an oven in the laboratory. With laboratory painted samples a factor that could cause error in the results was the speed and the force used with the applicator rod. The aim was to use a consistent and uniform method of application, but a possible human error in the process should be considered. The above mentioned factor affects mainly on the film thicknesses of the final product, which were monitored during the painting process and during the laboratory testing.

The PMT of the samples were measured during the oven cycle with a PMT-strip. Although the PMT was measured from a number of the samples, a measurement for all of the samples was not possible due to the large amount of samples. The oven had a temperature variation of approximately ± 3 °C and the oven cycle was automated so the potential varying of the PMT was quite small. The variations in temperature could cause insufficient evaporation of solvents or under-curing of the coating, possibly leading to some inconsistencies in the results.

As the substrate sheets were transported during winter time, the temperature of the sheets may have varied during the painting. As the painting process advanced, the sheets warmed and at some point reached room temperature. PMT strip was used randomly during the painting process; therefore the initial temperature of the sheet should not have had a significant effect on the PMT of the finished product.

The painted sheets were carefully selected and only the visibly intact sheets were painted. The inspection of the sheets was done during the painting process, so a number of scratches or impurities could be present in some of the sheets. Unnecessary handling of the sheets was minimized. Fingerprints and other such impurities might have an effect on the humidity resistance results or the adhesion of the coating.

Small paint jars were used in order to avoid the coagulation and sinking of pigments. A sufficient mixing of the paint was administered individually to each of the used paint jars. The mixing was done before each paint jar was first opened and mixing was performed also during the painting process. A notable amount of time went by between the first and the last sample painted with the same paint jar, so a possible sinking of the pigments might be a factor for some irregularities in the results.

## 8.3 Error due to the laboratory testing

Three different factors can alter the reliability of the results in this thesis. First factor for errors comes from the uncertainty of the measurements from the equipment and the methods used. Second factor governs the differences between the equipment used. Third

factor is human error caused by the person interpreting the results. The first factor was ignored due to the insignificant impact compared to the other factors.

Second factor was considered during the humidity testing, because two separate QCT cabinets were used. TOC 1 and TOC 2 were examined and interpreted separately so one QCT cabinet was used with the TOC 1 samples and the other for TOC 2 samples. The difference between the performances of the cabinets should not have therefore affected the results. QCT cabinets are sensitive and different exposure of humidity and temperature can be observed also within the cabinet. As the samples were evaluated in 250 h intervals, the difference between the exposures within the cabinet was minimized with a random placement of the samples after each interval.

Basically all of the testing methods used during the experimental part of this trial rely on the visual estimation of the sample. There was no direct numerical data to be gathered from the testing, so a factor of error comes from the person administering the tests. Only one person performed all of the tests and evaluated the results to minimize the human error during the testing. The results are therefore quite reliable and at least comparable to each other and between the different testing sets.

# 9. CONCLUSIONS

The main objective with this thesis was to find an optimal first layer of coating on top of two different thin organic coatings. The TOCs used in this thesis were selected beforehand with a separate testing and research work within SSAB. In the theoretical part of this thesis a backbone for the understanding of the coil coating process and the interactions between the TOCs and the first layer of coating were given. A brief introduction for the scientific principals associated with the adhesion between two coating layers was also given. The emphasis in the experimental part of this thesis was to find the most suitable combination of properties for the first coating layer. An extensive selection of different binders, film thicknesses and curing cycles were tested.

The selection for the optimal coating was done based on the humidity resistance and mechanical resistance of the coating. The testing in the experimental part had an emphasis on the adhesion between the TOC substrate and the first layer of the coating system. The TOC substrates were obtained from line trials of mass scale production. The different binder, film thickness and curing cycle combinations for the samples were done with a laboratory painting process. A statistical analysis, ANOVA, was used to determine the most optimal combinations of variables. As the analysis was a part of the thesis, an explanation of the said method was also provided.

In this chapter the conclusions from the test results and a discussion about the different observations that were done during the experimental part of the thesis are given. A separate subchapter provides a brief introduction to the related studies that were started according to the recommendation of this thesis.

## 9.1 Optimal first layer

The humidity resistance testing in QCT cabinets provided the basis for the selection of the optimal combination of the variables that were studied. Distinctive differences between the binders were observed. As explained earlier in the thesis the TOCs used in this thesis were quite different in composition, so both of the TOCs were studied separately.

As the MEK results gave a significant difference between the PVdF based binder mixtures, a conclusion was drawn that the binders with inferior results had obvious incompatibility issues with the TOC substrates. The incompatibility issues were not studied further as the 70 % PVDF and 30 % PMMA mixture gave promising results. Due to poor MEK results the 60/40 ratio PVdF based binders were eliminated, as inferior hu-

midity results could arise based on the poor solvent resistance. As mentioned the reason for the incompatibility was not studied, but most probably the improper preparation of the paint with 60/40 ratio between PVdF and PMMA itself was the reason for the poor results, since most of the paint companies are not producing it in daily business.

TOC 1 showed quite consistent and promising results with both the polyester based and the PVdF based binders. As QCT and mechanical testing results showed no obvious incompatibilities between the binders and the TOC 1, the TOC 1 substrate was ruled to be the more versatile and more compatible thin organic coating with different paint chemistries. Although more versatile with different paint chemistries TOC 1 samples showed inferior wet and dry adhesion properties. Even though the TOCs were not compared against each other, a notable observation should be considered that the TOC 2 gave slightly better results with the best possible coating system than the TOC 1, especially in QCT testing and wet and dry adhesion testing. Overall compatibility between the TOC and the different paint chemistries is considered to be significantly better for TOC 1 than TOC 2.

A clear notion on the incompatibility between the TOC 2 substrate and polyester based coating systems was observed throughout the entire process. Separate studies on the subject were started by Top Analytica and the manufacturer of the TOC as similar observations were done in this thesis and with the testing of the line trial material. A conclusion of the incompatibility of the polyester based coatings and the TOC 2 substrate was clear, but the reason for the incompatibility was studied further. A variety of different explanations for the phenomena surfaced during the thesis process. The manufacturer of the TOC also presented a product more suitable for polyester chemistry, which was not used in this thesis, but is further tested as a possibility for polyester based products in the future.

In the following, a discussion of the different possible reasons for the incompatibility issues is given. As almost all of the following reasons were studied further with separate research projects, only a plain explanation is given in this thesis. TOC 2 coating was concluded to have been under-cured during the line trial due to slightly too low temperatures in the convection ovens. The under-curing could have resulted in the poor compatibility issues between the polyester based binders and the TOC 2 coating. The optimal method of curing the TOC 2 was stated by the manufacturer to be done by rapid rise of the PMT at the first few seconds of the curing cycle. The rapid and aggressive rise of the PMT was not obtained during the line trial and the TOC 2 was left slightly under-cured. A separate study of post-curing the product obtained from the line trials was done, but a distinctive difference with compatibility of the polyester based binders was not achieved. Only marginally better MEK results were obtained from such post-curing of the product.

A discussion of the pH differences between the thin organic coating and the polyester based paints arose as the potential explanation of the incompatibilities. The TOC 2 product is strongly alkaline and the finished and cured surface of the coating is therefore also alkaline by nature. Polyester based products, except the A+I system, in this thesis are cured with an acid catalyzed reaction. All of the binders with acid catalyzed reactions gave poor MEK results and were for all practical purposes destroyed during the first 500 hours of QCT testing. For the purpose of understanding the phenomena a quick explanation of the problem is as follows. The difference in the pH of the TOC and the polyester based paint could have led to some unwanted reactions resulting in lower crosslinking levels than usually desired for the product. Under-curing of the product (waterborne) could also have led to trapped water in the TOC coating. When the first layer of the coating (polyester based) was cured in the laboratory oven, the trapped water from the TOC might have evaporated and reacted with the acid catalyst of the melamine crosslinker, resulting in hydrolysis of the achieved linkage. The possibility of said phenomena was discussed to be studied further, but because potential polyester based binder (A+I) was available for this thesis, the study was left out from the thesis.

The manufacturer of the TOC 2 did some further testing with the compatibility issues and came up with a few possible reasons for the problems addressed above. As the product was primarily designed for PVdF based top coats, the composition of the TOC itself might be the cause of the incompatibility issues. The TOC 2 was manufactured to have quite a high level of reactive groups in the surface, which promotes an excellent adhesion with PVdF based binders. The high level of reactive groups could leave a potential vulnerability to the polyester based products, because the polyester chemistry does not need as high level of reactive groups to adhere similar to the PVdF based chemistry. A potential solution for such problem was also discussed. A separate study was started that would test different PMT values in order to find the most suitable curing conditions in order to ensure the best possible adhesion between the TOC 2 and the polyester based binder. The theory behind the possibility for better compatibility with higher PMT lies in the much higher level of crosslinking achieved with the PMT raise. If the crosslinking level of the TOC 2 is raised with the higher PMT, the amount of reactive groups on the surface of the TOC 2 lowers, possibly offering a better adhesion between the products. A similar effect could be achieved with the post-curing of the product during the storage period. A notable post-curing was observed over a time period of two months, which lowered the amount of reactive groups on the surface of the product. Post-curing did not negatively affect the mechanical results of the product, but raised the MEK resistance slightly. Even with the slight increase in the MEK resistance, the product did not reach a satisfactory level.

With TOC 2 a wrinkling of the surface was observed with one of the polyester based binders (C+M). The wrinkling of the surface is sometimes a desired property for the coating, but was not supposed to happen with this specific coating layer. The mechani-

cal testing results were exceptionally good with this product, quite possibly due to the wrinkling effect, but the MEK results and QCT results revealed that the wrinkling was most probably a byproduct of some sort of problem during the curing. An explanation of the wrinkling might come from the previously mentioned incompatibility due to the pH difference. The explanation found in literature states that undesired wrinkling is usually a byproduct of uneven drying. When the surface of the applied film cures faster than the body of the film, a surface skin is formed and surface tension between the two curing phases (surface vs. body) creates distortion resulting in wrinkling. The exceptional mechanical results were probably due to the more flexible surface of the coating, which hid the real damage caused by the deformation. The poor adhesion became an issue during the QCT test when humidity entered between the coating and the TOC 2, resulting in an extensive blistering and eventually destruction of the coating.

The pretreatment layer and TOC layer play a notable role in the coating system. As seen from the subchapter 7.4 Test results from the second test set, a significant difference between the performances of the samples can be observed. With a plain HDG steel substrate none of the binders worked properly and significant amounts of deterioration and damage was observed. A clear conclusion on behalf of the pretreatment or TOC treatment can be made. With the comparison of the traditional pretreatment and the TOC based samples, as notable difference as seen between the HDG and traditional pretreatment was not observed. Some difference between the two methods was observed, but significant and clear conclusions could not be drawn. In both the mechanical and QCT testing done during this thesis, the best performance could be observed from the TOC based products. It should be noted that the traditional pretreatment is optimized to perform with a specific layer of primer, but in this thesis the pretreatment was used without the primer. Although in this thesis the TOC based products performed at least as well as the pretreatment products, the pretreatment product was not used as it optimally would be used. However in this case the results show quite promising performance for the TOC based products in coil coating industry. Research and development with the TOC based products is an ongoing and long-term project and this thesis was a small part of it.

The issues with the compatibility between the TOC 2 and polyester based binders resulted in an ongoing research. As the compatibility of the polyester chemistry and the TOC 2 is studied further, simultaneously the excellent compatibility with PVdF based binders opens a potential for future development and launching of the product. The results in this thesis and the results from the related studies done alongside the thesis can be considered guidelines towards future development projects. The HYBRIDS research program continues to tackle the issues with the TOC and in the future a TOC based product might provide an economical and an environmentally sound alternative for traditional color coated products.

## 9.2 Related TOC research projects

The studies with thin organic coatings continue with a collaboration of SSAB, the manufacturers of the TOC products and Top Analytica. In this subchapter the ongoing research project related to this thesis are listed.

In the future, if the TOC based products are used, the compatibility between the TOC surface and generally used backing coats should be confirmed. An ongoing research with the TOC 2 and epoxy based backing coats was started during the thesis project. So far the results from the studies show that epoxy backing coat can withstand the require amount of time when exposed to MEK and Stripper. The resistance against solvents gives a promising reassurance about the products capabilities as an alternative for pretreatment and primer.

Glueability and UV-radiation exposure testing of the TOC based products were started during the thesis project in order to establish a comprehensive knowledge of the different properties of the TOC based products.

A potential usage of the TOC based coating arose during the discussions between the manufacturer of the TOC 2, representatives of SSAB and Top Analytica. The use of fire retardant PIR-foams (polyisocyanurate) with coil coated products has been studied in order to find a possible product for sandwich panels for roofing and wall insulations. A recommendation for a research project about the adhesion between the TOC and the PIR-foam was thrown towards the manufacturer of the TOC 2. The study of the above mentioned subject is ongoing and finished results were not available before the publication of this thesis.

The TOC products performed with great potential in the line trials and in the consequent research projects such as this thesis and the above mentioned projects. As the research and development of the TOC based products continues and the possibilities for real customers are mapped, the future of the TOC based products looks extremely promising and could lead to several new product launches in different application segments of color coated steel.

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# APPENDIX 1: THICKNESS MEASURES

| 1. set of samples: Thickness measures (curing times, PMT range) | | | | | | |
|---|---|---|---|---|---|---|
| TOC 1 + POLYESTER BASED BINDERS | | | | | | |
| | Single curing (36s) (232 < PMT < 242) | | | Double curing (36s x 2) (232 < PMT < 242) | | |
| A + M | TARGET: 5µm | TARGET: 10µm | TARGET: 15µm | TARGET: 5µm | TARGET: 10µm | TARGET: 15µm |
| | 5.3 | 11.5 | 15 | 5 | 10.3 | 15.7 |
| | 5.6 | 10.7 | 14.8 | 5.1 | 10.2 | 15.4 |
| | 5.1 | 11.5 | 16.5 | 4.8 | 10.3 | 14.8 |
| | 5.8 | 10.1 | 15.5 | 5.2 | 10.1 | 15.0 |
| | Single curing (36s) (232 < PMT < 242) | | | Double curing (36s x 2) (232 < PMT < 242) | | |
| B + M | TARGET: 5µm | TARGET: 10µm | TARGET: 15µm | TARGET: 5µm | TARGET: 10µm | TARGET: 15µm |
| | 6.1 | 10.7 | 16.8 | 7.1 | 10.7 | 17.0 |
| | 6.5 | 10.5 | 17.1 | 5.8 | 10.2 | 17.4 |
| | 6.3 | 10.4 | 17.2 | 6.8 | 10.6 | 17.4 |
| | 7.0 | 10.5 | 17.0 | 6.2 | 10.4 | 17.3 |
| | Single curing (36s) (232 < PMT < 242) | | | Double curing (36s x 2) (232 < PMT < 242) | | |
| C + M | TARGET: 5µm | TARGET: 10µm | TARGET: 15µm | TARGET: 5µm | TARGET: 10µm | TARGET: 15µm |
| | 5.2 | 12.2 | 15.5 | 6.7 | 10.5 | 16.4 |
| | 7.2 | 10.5 | 16.2 | 6.2 | 11.4 | 15.2 |
| | 5.4 | 10.5 | 16.3 | 6.1 | 10.1 | 15.1 |
| | 6.0 | 11.6 | 16.4 | 7.2 | 10.4 | 16.0 |
| | Single curing (40s) (249 < PMT < 254) | | | Double curing (40s x 2) (249 < PMT < 254) | | |
| A + I | TARGET: 5µm | TARGET: 10µm | TARGET: 15µm | TARGET: 5µm | TARGET: 10µm | TARGET: 15µm |
| | 6.0 | 10.1 | 14.8 | 5.3 | 9.9 | 14.8 |
| | 5.7 | 9.7 | 16.0 | 6.6 | 10.1 | 14.6 |
| | 6.3 | 9.5 | 14.9 | 5.4 | 9.8 | 16.0 |
| | 6.3 | 10.3 | 15.1 | 6.2 | 9.9 | 14.7 |

| 1. set of samples: Thickness measures (curing times, PMT range) | | | | | | |
|---|---|---|---|---|---|---|
| TOC 1 + PVdF BASED BINDERS | | | | | | |
| | Single curing (40s) (249 < PMT < 254) | | | Double curing (40s x 2) (249 < PMT < 254) | | |
| 70/30 TS | TARGET: 5µm | TARGET: 10µm | TARGET: 15µm | TARGET: 5µm | TARGET: 10µm | TARGET: 15µm |
| | 5.1 | 9.8 | 15.0 | 5.4 | 9.7 | 14.9 |
| | 5.4 | 9.2 | 14.8 | 5.9 | 10.5 | 15.3 |
| | 5.3 | 9.5 | 14.9 | 5.6 | 10.1 | 15.1 |
| | Single curing (40s) (249 < PMT < 254) | | | Double curing (40s x 2) (249 < PMT < 254) | | |
| 70/30 TP | TARGET: 5µm | TARGET: 10µm | TARGET: 15µm | TARGET: 5µm | TARGET: 10µm | TARGET: 15µm |
| | 5.8 | 10.6 | 15.4 | 5.9 | 10.5 | 15.1 |
| | 5.5 | 10.3 | 15.7 | 5.7 | 10.8 | 15.6 |
| | 5.7 | 10.5 | 15.5 | 5.8 | 10.6 | 15.3 |
| | Single curing (40s) (249 < PMT < 254) | | | Double curing (40s x 2) (249 < PMT < 254) | | |
| 60/40 TP | TARGET: 5µm | TARGET: 10µm | TARGET: 15µm | TARGET: 5µm | TARGET: 10µm | TARGET: 15µm |
| | 5.4 | 10.1 | 14.3 | 5.5 | 11.3 | 14.1 |
| | 5.4 | 9.8 | 14.0 | 5.3 | 11.3 | 14.1 |
| | 5.4 | 9.9 | 14.1 | 5.4 | 11.3 | 14.1 |
| | Single curing (40s) (249 < PMT < 254) | | | Double curing (40s x 2) (249 < PMT < 254) | | |
| 60/40 TS | TARGET: 5µm | TARGET: 10µm | TARGET: 15µm | TARGET: 5µm | TARGET: 10µm | TARGET: 15µm |
| | 6.0 | 11.0 | 15.6 | 5.3 | 11.0 | 14.1 |
| | 5.7 | 10.3 | 14.7 | 6.0 | 11.0 | 15.0 |
| | 5.8 | 10.6 | 15.1 | 5.7 | 11.0 | 14.5 |

| 1. set of samples: Thickness measures (curing times, PMT range) | | | | | | |
|---|---|---|---|---|---|---|
| TOC 2 + POLYESTER BASED BINDERS | | | | | | |
| | Single curing (36s) (232 < PMT < 242) | | | Double curing (36s x 2) (232 < PMT < 242) | | |
| A + M | TARGET: 5µm | TARGET: 10µm | TARGET: 15µm | TARGET: 5µm | TARGET: 10µm | TARGET: 15µm |
| | 7.5 | 13.6 | 16.8 | 7.5 | 12.5 | 19.0 |
| | 7.9 | 12.3 | 17.6 | 6.7 | 13.3 | 18.5 |
| | 7.2 | 12.7 | 18.7 | 7.9 | 12.6 | 17.5 |
| | 7.7 | 12.3 | 17.4 | 6.4 | 12.0 | 17.9 |
| | Single curing (36s) (232 < PMT < 242) | | | Double curing (36s x 2) (232 < PMT < 242) | | |
| B + M | TARGET: 5µm | TARGET: 10µm | TARGET: 15µm | TARGET: 5µm | TARGET: 10µm | TARGET: 15µm |
| | 7.9 | 13.4 | 20.5 | 8.0 | 12.8 | 19.6 |
| | 7.8 | 13.4 | 19.5 | 7.4 | 13.8 | 20.3 |
| | 8.0 | 13.9 | 20.7 | 7.6 | 13.4 | 18.6 |
| | 7.9 | 14.0 | 19.0 | 8.2 | 13.0 | 18.3 |
| | Single curing (36s) (232 < PMT < 242) | | | Double curing (36s x 2) (232 < PMT < 242) | | |
| C + M | TARGET: 5µm | TARGET: 10µm | TARGET: 15µm | TARGET: 5µm | TARGET: 10µm | TARGET: 15µm |
| | 8.2 | 13.8 | 17.7 | 8.7 | 13.4 | 16.9 |
| | 8.4 | 13.4 | 17.2 | 8.8 | 13.0 | 17.4 |
| | 7.3 | 12.8 | 17.8 | 8.8 | 13.2 | 16.8 |
| | 8.0 | 12.7 | 17.7 | 8.9 | 13.2 | 17.0 |
| | Single curing (40s) (249 < PMT < 254) | | | Double curing (40s x 2) (249 < PMT < 254) | | |
| A + I | TARGET: 5µm | TARGET: 10µm | TARGET: 15µm | TARGET: 5µm | TARGET: 10µm | TARGET: 15µm |
| | 7.0 | 12.3 | 16.6 | 7.8 | 12.9 | 16.8 |
| | 6.8 | 12.5 | 16.4 | 7.4 | 12.7 | 17.0 |
| | 7.1 | 12.2 | 16.6 | 6.1 | 13.0 | 16.5 |
| | 7.5 | 12.1 | 16.7 | 6.5 | 13.9 | 16.4 |

| 1. set of samples: Thickness measures (curing times, PMT range) | | | | | | |
|---|---|---|---|---|---|---|
| TOC 2 + PVdF BASED BINDERS | | | | | | |
| | Single curing (40s) (249 < PMT < 254) | | | Double curing (40s x 2) (249 < PMT < 254) | | |
| 70/30 TS | TARGET: 5µm | TARGET: 10µm | TARGET: 15µm | TARGET: 5µm | TARGET: 10µm | TARGET: 15µm |
| | 6.9 | 9.0 | 15.0 | 5.9 | 10.7 | 15.0 |
| | 6.3 | 10.9 | 15.5 | 5.2 | 10.3 | 15.4 |
| | 6.6 | 9.9 | 15.3 | 5.5 | 10.5 | 15.2 |
| | Single curing (40s) (249 < PMT < 254) | | | Double curing (40s x 2) (249 < PMT < 254) | | |
| 70/30 TP | TARGET: 5µm | TARGET: 10µm | TARGET: 15µm | TARGET: 5µm | TARGET: 10µm | TARGET: 15µm |
| | 6.4 | 10.8 | 15.6 | 6.3 | 11.1 | 15.0 |
| | 6.6 | 11.2 | 16.3 | 5.8 | 11.2 | 14.7 |
| | 6.5 | 11.0 | 16.0 | 6.1 | 11.1 | 14.9 |
| | Single curing (40s) (249 < PMT < 254) | | | Double curing (40s x 2) (249 < PMT < 254) | | |
| 60/40 TP | TARGET: 5µm | TARGET: 10µm | TARGET: 15µm | TARGET: 5µm | TARGET: 10µm | TARGET: 15µm |
| | 5.6 | 11.1 | 15.1 | 5.3 | 12.0 | 16.0 |
| | 6.3 | 11.5 | 15.8 | 5.8 | 11.2 | 15.7 |
| | 6.0 | 11.3 | 15.4 | 5.5 | 11.6 | 15.8 |
| | Single curing (40s) (249 < PMT < 254) | | | Double curing (40s x 2) (249 < PMT < 254) | | |
| 60/40 TS | TARGET: 5µm | TARGET: 10µm | TARGET: 15µm | TARGET: 5µm | TARGET: 10µm | TARGET: 15µm |
| | 6.2 | 10.7 | 15.5 | 5.9 | 11.2 | 15.9 |
| | 6.3 | 10.4 | 15.6 | 6.7 | 10.5 | 15.2 |
| | 6.3 | 10.6 | 15.6 | 6.3 | 10.9 | 15.5 |

# APPENDIX 2: IMPACT RESISTANCE RESULTS

| | TOC 1 | | | | TOC 2 | | | |
|---|---|---|---|---|---|---|---|---|
| A+M | Single curing | IMPACT | double curing | IMPACT | Single curing | IMPACT | double curing | IMPACT |
| | 5 µm | 13 | 5 µm | 14 | 5 µm | 15 | 5 µm | 13.5 |
| | 10 µm | 10.5 | 10 µm | 14.5 | 10 µm | 9.5 | 10 µm | 11.5 |
| | 15 µm | 8.5 | 15 µm | 7 | 15 µm | 6.5 | 15 µm | 6.5 |
| B+M | Single curing | IMPACT | double curing | IMPACT | Single curing | IMPACT | double curing | IMPACT |
| | 5 µm | 9 | 5 µm | 9.5 | 5 µm | 7.5 | 5 µm | 9 |
| | 10 µm | 6 | 10 µm | 6.5 | 10 µm | 5 | 10 µm | 4 |
| | 15 µm | 4 | 15 µm | 4.5 | 15 µm | 4 | 15 µm | 4 |
| C+M | Single curing | IMPACT | double curing | IMPACT | Single curing | IMPACT | double curing | IMPACT |
| | 5 µm | 8.5 | 5 µm | 8.5 | 5 µm | 10 | 5 µm | 8.5 |
| | 10 µm | 8.5 | 10 µm | 5.5 | 10 µm | 5.5 | 10 µm | 6 |
| | 15 µm | 4.5 | 15 µm | 4.5 | 15 µm | 6 | 15 µm | 6 |
| A+I | Single curing | IMPACT | double curing | IMPACT | Single curing | IMPACT | double curing | IMPACT |
| | 5 µm | 10 | 5 µm | 9.5 | 5 µm | 13.5 | 5 µm | 10.5 |
| | 10 µm | 8 | 10 µm | 10.5 | 10 µm | 12.5 | 10 µm | 8.5 |
| | 15 µm | 12.5 | 15 µm | 7.5 | 15 µm | 11 | 15 µm | 11.5 |
| 70/30 TS | Single curing | IMPACT | double curing | IMPACT | Single curing | IMPACT | double curing | IMPACT |
| | 5 µm | 11.5 | 5 µm | 8.5 | 5 µm | 8.5 | 5 µm | 7.5 |
| | 10 µm | 6 | 10 µm | 7.5 | 10 µm | 7 | 10 µm | 9.5 |
| | 15 µm | 4.5 | 15 µm | 5.5 | 15 µm | 8.5 | 15 µm | 8.5 |
| 70/30 TP | Single curing | IMPACT | double curing | IMPACT | Single curing | IMPACT | double curing | IMPACT |
| | 5 µm | 8 | 5 µm | 9 | 5 µm | 16.5 | 5 µm | 10.5 |
| | 10 µm | 5.5 | 10 µm | 4.5 | 10 µm | 11.5 | 10 µm | 7 |
| | 15 µm | 4.5 | 15 µm | 4 | 15 µm | 6 | 15 µm | 6 |
| 60/40 TS | Single curing | IMPACT | double curing | IMPACT | Single curing | IMPACT | double curing | IMPACT |
| | 5 µm | 8.5 | 5 µm | 8 | 5 µm | 13.5 | 5 µm | 10 |
| | 10 µm | 7.5 | 10 µm | 4 | 10 µm | 10 | 10 µm | 8 |
| | 15 µm | 5.5 | 15 µm | 5 | 15 µm | 6 | 15 µm | 6 |
| 60/40 TP | Single curing | IMPACT | double curing | IMPACT | Single curing | IMPACT | double curing | IMPACT |
| | 5 µm | 9.5 | 5 µm | 8 | 5 µm | 13 | 5 µm | 11 |
| | 10 µm | 5.5 | 10 µm | 5.5 | 10 µm | 9 | 10 µm | 8 |
| | 15 µm | 4.5 | 15 µm | 4 | 15 µm | 7 | 15 µm | 5.5 |
| | TOC 1 | | | | TOC 2 | | | |

# APPENDIX 3: T-BEND RESULTS

| | TOC 1 | | | | | | TOC 2 | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A+M | Single curing | T-Bend | Adhesion | double curing | T-Bend | Adhesion | Single curing | T-Bend | Adhesion | double curing | T-Bend | Adhesion |
| | 5 µm | 2.36 | 0 | 5 µm | 2.44 | 0 | 5 µm | 2.14 | 1.51 | 5 µm | 2.52 | 1.62 |
| | 10 µm | 1.94 | 0 | 10 µm | 1.4 | 0 | 10 µm | 1.51 | 1.12 | 10 µm | 1.84 | 0.58 |
| | 15 µm | 1.46 | 0 | 15 µm | 1 | 0 | 15 µm | 0 | 0 | 15 µm | 0.62 | 0 |
| B+M | Single curing | T-Bend | Adhesion | double curing | T-Bend | Adhesion | Single curing | T-Bend | Adhesion | double curing | T-Bend | Adhesion |
| | 5 µm | 2.2 | 0.88 | 5 µm | 1.65 | 0.42 | 5 µm | 1.66 | 1.52 | 5 µm | 1.5 | 1.33 |
| | 10 µm | 1.69 | 0.16 | 10 µm | 2.3 | 0 | 10 µm | 0 | 0 | 10 µm | 0.36 | 0 |
| | 15 µm | 1.24 | 0 | 15 µm | 2.22 | 0 | 15 µm | 0 | 0 | 15 µm | 0 | 0 |
| C+M | Single curing | T-Bend | Adhesion | double curing | T-Bend | Adhesion | Single curing | T-Bend | Adhesion | double curing | T-Bend | Adhesion |
| | 5 µm | 1.82 | 0 | 5 µm | 2.36 | 0 | 5 µm | 2.83 | 1.06 | 5 µm | 1.72 | 0 |
| | 10 µm | 1.39 | 0 | 10 µm | 1.52 | 0 | 10 µm | 1.36 | 0 | 10 µm | 0.62 | 0 |
| | 15 µm | 0.67 | 0 | 15 µm | 1.24 | 0 | 15 µm | 0.5 | 0 | 15 µm | 0 | 0 |
| A+I | Single curing | T-Bend | Adhesion | double curing | T-Bend | Adhesion | Single curing | T-Bend | Adhesion | double curing | T-Bend | Adhesion |
| | 5 µm | 3.88 | 0 | 5 µm | 3.1 | 0 | 5 µm | 3.05 | 0.73 | 5 µm | 2.78 | 1.7 |
| | 10 µm | 1.66 | 0 | 10 µm | 2.06 | 0 | 10 µm | 0.93 | 0 | 10 µm | 1.27 | 0.63 |
| | 15 µm | 0.8 | 0 | 15 µm | 1.78 | 0 | 15 µm | 0.53 | 0 | 15 µm | 1.09 | 0 |
| 70/30 TS | Single curing | T-Bend | Adhesion | double curing | T-Bend | Adhesion | Single curing | T-Bend | Adhesion | double curing | T-Bend | Adhesion |
| | 5 µm | 2 | 0.66 | 5 µm | 1.66 | 0 | 5 µm | 2.99 | 0.31 | 5 µm | 2.59 | 0 |
| | 10 µm | 1.81 | 0 | 10 µm | 1.51 | 0 | 10 µm | 1.18 | 0 | 10 µm | 1.97 | 0 |
| | 15 µm | 0.67 | 0 | 15 µm | 0.52 | 0 | 15 µm | 0.7 | 0 | 15 µm | 0.48 | 0 |
| 70/30 TP | Single curing | T-Bend | Adhesion | double curing | T-Bend | Adhesion | Single curing | T-Bend | Adhesion | double curing | T-Bend | Adhesion |
| | 5 µm | 2.54 | 0.3 | 5 µm | 3 | 0.39 | 5 µm | 1.34 | 0 | 5 µm | 1.76 | 0.66 |
| | 10 µm | 2.31 | 0 | 10 µm | 2.41 | 0 | 10 µm | 0.98 | 0 | 10 µm | 0.37 | 0 |
| | 15 µm | 1.46 | 0 | 15 µm | 1.16 | 0 | 15 µm | 0.44 | 0 | 15 µm | 0.12 | 0 |
| 60/40 TS | Single curing | T-Bend | Adhesion | double curing | T-Bend | Adhesion | Single curing | T-Bend | Adhesion | double curing | T-Bend | Adhesion |
| | 5 µm | 2.36 | 0 | 5 µm | 2.19 | 0 | 5 µm | 3.16 | 0 | 5 µm | 2.81 | 0 |
| | 10 µm | 1.54 | 0 | 10 µm | 1.42 | 0 | 10 µm | 1.51 | 0 | 10 µm | 1.46 | 0 |
| | 15 µm | 0.88 | 0 | 15 µm | 0.83 | 0 | 15 µm | 0.59 | 0 | 15 µm | 0.96 | 0 |
| 60/40 TP | Single curing | T-Bend | Adhesion | double curing | T-Bend | Adhesion | Single curing | T-Bend | Adhesion | double curing | T-Bend | Adhesion |
| | 5 µm | 2.57 | 0.56 | 5 µm | 2.41 | 0.53 | 5 µm | 2.7 | 0.39 | 5 µm | 2.68 | 0.29 |
| | 10 µm | 1.35 | 0 | 10 µm | 1.1 | 0 | 10 µm | 1.76 | 0 | 10 µm | 1.48 | 0 |
| | 15 µm | 0.61 | 0 | 15 µm | 1.01 | 0 | 15 µm | 0.62 | 0 | 15 µm | 0.43 | 0 |
| | TOC 1 | | | | | | TOC 2 | | | | | |

# APPENDIX 4: QCT RESULTS

| Sample (Polyester) | Curing [1x, 2x] | Thickness [µm] | TOC 1 | | | |
|---|---|---|---|---|---|---|
| | | | 250 h | 500 h | 750 h | 1000 h |
| A+I | 1x | 5 | 3s2 | 4s2 | 4s2 | 4s2 |
| A+I | 1x | 10 | 4s2 | 4s2 | 4s2 | 4s2 |
| A+I | 1x | 15 | 4s2 | 5s2 | 5s2 | 5s2 |
| A+I | 2x | 5 | 3s2 | 3s2 | 3s2 | 3s2 |
| A+I | 2x | 10 | 3s2 | 3s2 | 3s2 | 3s2 |
| A+I | 2x | 15 | 4s2 | 4s2 | 4s2 | 4s2 |
| A+M | 1x | 5 | 4s2 / 5s2 | 5s2 | 5s2 | 5s2 |
| A+M | 1x | 10 | 4s2 | 5s2 | 5s2 | 5s2 |
| A+M | 1x | 15 | 5s2 | 5s2 + *s3 | 5s2 + *s3 | 5s2 + *s3 |
| A+M | 2x | 5 | 4s2 / 5s2 | 5s2 | 5s2 | 5s2 |
| A+M | 2x | 10 | 4s2 | 5s2 | 5s2 | 5s2 |
| A+M | 2x | 15 | 4s2 | 5s2 | 5s2 | 5s2 |
| B+M | 1x | 5 | 5s2 | 5s2 / 3s3 | 5s3 | 5s3 |
| B+M | 1x | 10 | 2s3 | 5s3 | 5s3 | 5s3 |
| B+M | 1x | 15 | 5s2 + *s3 | 5s4 | 5s4 | 5s4 |
| B+M | 2x | 5 | 4s2 | 5s2 | 5s2 | 5s2 |
| B+M | 2x | 10 | 5s2 + *s3 | 5s3 | 5s3 | 5s3 |
| B+M | 2x | 15 | 4s3 | 4s4 | 4s4 | 4s4 |
| C+M | 1x | 5 | 5s2 | 5s2 | 5s2 | 5s2 |
| C+M | 1x | 10 | 5s2 + *s3 | 5s2 + *s3 | 5s2 + *s3 | 5s2 + *s3 |
| C+M | 1x | 15 | 5s2 | 5s2 | 5s2 | 5s2 |
| C+M | 2x | 5 | 5s2 | 5s2 | 5s2 | 5s2 |
| C+M | 2x | 10 | 5s2 / 4s2 | 5s2 | 5s2 | 5s2 |
| C+M | 2x | 15 | 4s2 | 5s2 | 5s2 | 5s2 |

| Sample (PVDF) | Curing [1x, 2x] | Thickness [µm] | TOC 1 | | | |
|---|---|---|---|---|---|---|
| | | | 250 h | 500 h | 750 h | 1000 h |
| 60/40 TP | 1x | 5 | 5s2 | 5s2 | 5s2 | 5s2 |
| 60/40 TP | 1x | 10 | 4s2 | 5s2 | 5s2 | 5s2 |
| 60/40 TP | 1x | 15 | 3s2 | 3s2 | 3s2 | 4s2 |
| 60/40 TP | 2x | 5 | 5s2 | 5s2 | 5s2 | 5s2 |
| 60/40 TP | 2x | 10 | 4s2 | 5s2 | 5s2 | 5s2 |
| 60/40 TP | 2x | 15 | 2s2 | 3s2 | 3s2 | 4s2 |
| 60/40 TS | 1x | 5 | 5s2 | 5s2 | 5s2 | 5s2 |
| 60/40 TS | 1x | 10 | 3s2 | 4s2 | 4s2 | 5s2 |
| 60/40 TS | 1x | 15 | 3s2 | 4s2 | 4s2 | 4s2 |
| 60/40 TS | 2x | 5 | 5s2 | 5s2 | 5s2 | 5s2 |
| 60/40 TS | 2x | 10 | 3s2 | 4s2 | 4s2 | 5s2 |
| 60/40 TS | 2x | 15 | 2s2 | 4s2 | 4s2 | 4s2 |
| 70/30 TP | 1x | 5 | 3s2 | 3s2 | 4s2 | 5s2 |
| 70/30 TP | 1x | 10 | 3s2 | 3s2 | 3s2 | 3s2 |
| 70/30 TP | 1x | 15 | 2s2 | 2s2 | 2s2 | 2s2 |
| 70/30 TP | 2x | 5 | 3s2 | 3s2 | 4s2 | 4s2 |
| 70/30 TP | 2x | 10 | 3s2 | 3s2 | 3s2 | 3s2 |
| 70/30 TP | 2x | 15 | 2s2 | 2s2 | 2s2 | 2s2 |
| 70/30 TS | 1x | 5 | 3s2 | 3s2 | 3s2 | 3s2 |
| 70/30 TS | 1x | 10 | 2s2 | 2s2 | 2s2 | 2s2 |
| 70/30 TS | 1x | 15 | 0 | 0 | 0 | 0 |
| 70/30 TS | 2x | 5 | 3s2 | 3s2 | 4s2 | 4s2 |
| 70/30 TS | 2x | 10 | 0 | 0 | 0 | 0 |
| 70/30 TS | 2x | 15 | 0 | 0 | 0 | 0 |

* singular spot with the corresponding damage

| Sample (Polyester) | Curing [1x, 2x] | Thickness [µm] | TOC 2 | | | |
|---|---|---|---|---|---|---|
| | | | 250 h | 500 h | 750 h | 1000 h |
| A+I | 1x | 5 | 0 | 0 | 0 | 0 |
| A+I | 1x | 10 | 0 | 0 | 0 | 0 |
| A+I | 1x | 15 | 0 | 0 | 0 | 0 |
| A+I | 2x | 5 | 0 | 0 | 0 | 0 |
| A+I | 2x | 10 | 0 | 0 | 0 | 0 |
| A+I | 2x | 15 | 0 | 0 | 0 | 0 |
| A+M | 1x | 5 | X | x | POISTETTU KAAPISTA | |
| A+M | 1x | 10 | X + ** 5s3 | x | | |
| A+M | 1x | 15 | 5s3, 2s5 | x | | |
| A+M | 2x | 5 | X | x | | |
| A+M | 2x | 10 | 5s3, 2s4 | x | | |
| A+M | 2x | 15 | 5s2, 4s3 | x | | |
| B+M | 1x | 5 | X | x | POISTETTU KAAPISTA | |
| B+M | 1x | 10 | 3s5, 5s3 | x | | |
| B+M | 1x | 15 | 0 + ** 4s3 | 5s3, 2s5 | | |
| B+M | 2x | 5 | X | x | | |
| B+M | 2x | 10 | 0 | x | | |
| B+M | 2x | 15 | 0 | 5s3 | | |
| C+M | 1x | 5 | 4s4, 2s5 | x | POISTETTU KAAPISTA | |
| C+M | 1x | 10 | 4s5 | x | | |
| C+M | 1x | 15 | 5s3 | 5s4 | | |
| C+M | 2x | 5 | 4s3 | x | | |
| C+M | 2x | 10 | 3s2, 3s3 | x | | |
| C+M | 2x | 15 | 3s2, 4s2 | 5s4 | | |

| Sample (PVDF) | Curing [1x, 2x] | Thickness [µm] | TOC 2 | | | |
|---|---|---|---|---|---|---|
| | | | 250 h | 500 h | 750 h | 1000 h |
| 60/40 TP | 1x | 5 | 0 + * s2 | 2s2 | 2s2 | 3s2 |
| 60/40 TP | 1x | 10 | 0 | 0 | 2s2 | 3s2 |
| 60/40 TP | 1x | 15 | 0 | 0 | 2s2 | 3s2 |
| 60/40 TP | 2x | 5 | 0 | 0 | 2s2 | 2s2 |
| 60/40 TP | 2x | 10 | 0 | 0 | 2s2 | 3s2 |
| 60/40 TP | 2x | 15 | 0 | 0 | 2s2 | 2s2 |
| 60/40 TS | 1x | 5 | 0 + * s2 | 2s2 | 4s2 | 5s2 |
| 60/40 TS | 1x | 10 | 0 | 3s2 | 3s2 | 4s2 |
| 60/40 TS | 1x | 15 | 0 | 0 | 3s2 | 3s2 |
| 60/40 TS | 2x | 5 | 0 | 0 | 3s2 | 3s3 |
| 60/40 TS | 2x | 10 | 0 | 0 | 2s2 | 2s3 |
| 60/40 TS | 2x | 15 | 0 + * s2 | 3s2 | 3s2 | 3s2 |
| 70/30 TP | 1x | 5 | 0 | 0 | 0 | 0 |
| 70/30 TP | 1x | 10 | 0 | 0 | 0 | 0 |
| 70/30 TP | 1x | 15 | 0 + ** 3s2 | 0 + ** 3s2 | 0 + ** 3s2 | 0 + ** 3s2 |
| 70/30 TP | 2x | 5 | 0 | 0 | 0 | 0 |
| 70/30 TP | 2x | 10 | 0 | 0 | 0 | 0 |
| 70/30 TP | 2x | 15 | 0 | 0 | 0 | 0 |
| 70/30 TS | 1x | 5 | 0 | 0 | 2s2 | 2s2 |
| 70/30 TS | 1x | 10 | 0 + *s2 | 0 + *s2 | 3s2 | 5s2 |
| 70/30 TS | 1x | 15 | 0 + ** 2s4 | 0 + ** 2s4 | 3s2 + ** 2s4 | 3s2 + **2s4 |
| 70/30 TS | 2x | 5 | 0 + *s2 | 0 + *s2 | 3s2 | 3s3 |
| 70/30 TS | 2x | 10 | 0 | 0 | 2s2 | 4s2 |
| 70/30 TS | 2x | 15 | 0 | 0 | 3s2 | 4s2 + *s5 |

* singular spot with the corresponding damage, ** a clear stain with corresponding damage

# APPENDIX 5: RESULTS FOR THE FINAL SERIES

| Substrate | Binder | Curing [1x, 2x] | Thickness [µm] | T-Bend (flexibility / loss of adhesion) [T] | Impact resistance [from 4 to 20] |
|---|---|---|---|---|---|
| TOC 1 | C+M | 1x | 15 | 0 / 0 | 4 |
| Pre-treatment | C+M | 1x | 15 | 0 / 0 | 5 |
| HDG | C+M | 1x | 15 | 0 / 0 | 7 |
| TOC 1 | 70/30 TS | 1x | 15 | 0.4 / 0 | 4.5 |
| Pre-treatment | 70/30 TS | 1x | 15 | 1.3 / 0 | 8 |
| HDG | 70/30 TS | 1x | 15 | 2.2 / 0 | 11.5 |
| TOC 2 | A+I | 2x | 15 | 0.8 / 0 | 6.5 |
| Pre-treatment | A+I | 2x | 15 | 0.4 / 0 | 6 |
| HDG | A+I | 2x | 15 | 0.3 / 0 | 6 |
| TOC 2 | 70/30 TP | 2x | 15 | 0 / 0 | 4.5 |
| Pre-treatment | 70/30 TP | 2x | 15 | 0.2 / 0 | 4.5 |
| HDG | 70/30 TP | 2x | 15 | 0.5 / 0 | 9 |

| Substrate | Binder | Curing [1x, 2x] | Thickness [µm] | 250 h | 500 h | 750 h | 1000 h |
|---|---|---|---|---|---|---|---|
| TOC 1 | C+M | 1x | 15 | 3s2 | 4s2 | 5s2 | 5s2 |
| Pretreatment | C+M | 1x | 15 | 4s2 | 5s2 | 5s2 | 5s2 |
| HDG | C+M | 1x | 15 | 5s2 / 4s3 | 4s3 | 3s4 | 5s4 |
| TOC 1 | 70/30 TS | 1x | 15 | 0 | 0 | 2s2 | 3s2 |
| Pretreatment | 70/30 TS | 1x | 15 | 0 + * s2 | 2s2 | 2s2 | 2s2 |
| HDG | 70/30 TS | 1x | 15 | 4s3 | 5s3 + *s4 | 3s4 | 5s4 |
| TOC 2 | A+I | 2x | 15 | 0 | 0 | 0 | 0 |
| Pretreatment | A+I | 2x | 15 | 4s2 | 5s2 | 5s2 | 5s2 |
| HDG | A+I | 2x | 15 | 5s2 / 2s3 | 4s3 | 4s3 | 5s3 / 5s4 |
| TOC 2 | 70/30 TP | 2x | 15 | 0 | 0 | 0 | 2s2 |
| Pre-treatment | 70/30 TP | 2x | 15 | 0 + * s2 | 2s2 | 2s2 | 2s2 |
| HDG | 70/30 TP | 2x | 15 | 2s2 + **5s2 | 3s2 + **3s3 | 3s2+ **3s3 | 3s3 |

* singular spot with the corresponding damage ** a clear stain with corresponding damage

** a clear stain with corresponding damage